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Metallic nanostructures, ultrathin films and optical technologies for hydrogen storage and switchable mirrors

Chung-Kiak Poh
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Metallic nanostructures, ultrathin films and optical technologies for hydrogen storage and switchable mirrors

A thesis submitted in fulfillment of the requirements for the award of the degree

Doctor of Philosophy

from

University of Wollongong

by

Chung-Kiak Poh (BSc. Hons., MEng. Sci.)

Institute for Superconducting and Electronic Materials

2011
DECLARATION

I, Chung-Kiak Poh, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, at the Institute for Superconducting and Electronic Materials, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Chung-Kiak Poh

May 18, 2011
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Furthermore, I would like to acknowledge the technical assistance of Mr. Ronald Kinnell and Mr. Robert Morgan for their part in the construction of the customized hydrogen hermetic optical cell, which is central to the work reported in this thesis. I would also like to thank Ms. Crystal Longin for her generous help. I humbly thank all my friends, colleagues, and staff members, in particular Dr. Konstantin Konstantinov and Dr. Rong Zeng, who have made my time at ISEM so much richer and more fulfilling.
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The ability of some hydrides to reversibly absorb hydrogen under the right conditions makes them potential candidates for hydrogen storage, while the change in electrical or optical properties during the metal-insulator transition can be used to realize devices of technological interests such as two-dimensional hydrogen diffusion indicators and smart windows.

This thesis focuses primarily on the investigation of metal hydrides based on magnesium and palladium, in the form of both nanopowders and thin films. In general, samples prepared in the form of nanopowders were intended for hydrogen storage applications, while samples prepared in the form of thin film were intended for switchable mirror applications. Nanopowder samples were synthesized by ball milling, while the thin films were prepared by physical vapor deposition techniques such as pulsed laser deposition and thermal evaporation.

The desorption capacity, thermodynamics, and kinetics of Ti- and Ni/Ti-catalyzed Mg hydrides were investigated using Sieverts-type apparatus and differential scanning calorimetry. Based on analysis of the van’t Hoff equation and the Kissinger equation, the addition of Ti and Ni as catalysts has been found to play a key role in improving the thermodynamic and kinetic properties of magnesium hydride by decreasing the desorption temperature and the activation energy. A combination of Ti and Ni is a more effective catalyst than either Ti or Ni alone, suggesting the existence of a synergetic effect.
We propose and demonstrate a simple but effective real-time optical method to determine the $T_{\text{des}}$ and kinetics of freshly fabricated magnesium nanowires inside a transparent quartz tube, while it is still under the protective gas environment. The proposed characterization technique based on optical reflection requires only milligrams of sample and helps to eliminate the common problem of oxidation associated with removal and transport of the freshly fabricated nanostructures into an inert protective environment. This optical technique could be applied to any hydrogen storage material in powder form which shows a significant difference in its optical absorption between the hydride and the non-hydride phase. A three-color, 8-bit, $240 \times 320$ pixel imager was used to acquire the optical signals, and the image processing was performed in MATLAB®.

Magnesium films of various thicknesses were fabricated by pulsed laser deposition and capped with a palladium protective layer. The change in the kinetics as a function of film thickness was measured. Raman spectroscopy on the 11 nm magnesium hydride film reveals a small but detectable peak arising from the $E_g$ phonon mode. The Raman frequencies of bulk magnesium hydride predicted by CASTEP calculations are included for comparison.
We propose and demonstrate a multi-stacked structure intended for low-nanometer ultrathin films of various metal hydrides, which would enable them to simultaneously achieve an enhanced optical contrast equivalent to that of thicker films, yet be able to retain much of the rapid switching kinetics characteristic of low-nanometer ultrathin films. Such improvement in the performance will help to further extend the scope of applications, particularly in the area of dynamic switchable mirrors, where switching speed and high switching contrast are crucial.

Future work will also be based on resonant photodesorption of hydrogen, as well as surface plasmon nanophotonics, both of which are aimed at improving the efficiency of hydrogen desorption of promising hydrides such as MgH$_2$ or LiBH$_4$. 
CHAPTER 1

Introduction

Hydrogen as a chemical element was discovered by Henry Cavendish in 1766 and has been used in a variety of ways ever since, but it is only in the past three decades or so that its potential as an energy carrier has gradually emerged [1]. An extensive global reliance on fossil fuels such as coal and crude oil as energy sources has led to a number of unprecedented challenges facing humankind, such as global warming due to the release of enormous amount of carbon dioxide, changes in climate which affect crops and vegetation, and poor urban air quality.

Hydrogen is an attractive alternative energy carrier for replacing our current fossil fuel-based economy. The future hydrogen economy is envisioned to offer solutions to the global energy requirements, while simultaneously reducing emissions of carbon dioxide and other greenhouse gases. Hydrogen is non-toxic and can be made from water using electricity from renewable sources such as wind and solar. Used in fuel cells, hydrogen generates electricity and emits only water as the by-product. Fuel cells can be made in various sizes, ranging from the miniature ones that power laptop computers to large power plants [2].

There are, however, obstacles to the hydrogen economy, and one of them relates to the safe and efficient storage of hydrogen, particularly for mobile/automotive applications. From all the possible solutions to hydrogen storage that have been researched so far, storage in solid media (hydrides) appears to be the most promising in the long run.
Advances in nanoscience and technology will inevitably allow hydride materials with characteristics that can fulfill at least the basic requirements for hydrogen storage.

The two most researched materials for hydrogen storage are magnesium and palladium. Magnesium is attractive because it is abundant, inexpensive, and relatively benign to the environment. However, one drawback of bulk magnesium is that it releases hydrogen at around 300°C, and the hydrogen release rate is slow.

Given the promise of magnesium as a hydrogen storage material, this thesis thus focuses primarily on research into ways to reduce the hydrogen desorption temperature of magnesium, as well as improving its kinetics.

On par with the development of hydrogen storage materials, fast and effective hydrogen gas detection sensors are also important for the full implementation of the hydrogen economy. The final part of this thesis explores the possibility of developing fast switchable mirrors based on ultrathin films of hydride. Palladium ultrathin film in a multi-stacked configuration is used in the demonstration experiment.

Two methods are used in this thesis for material preparation, namely, ball milling for nanostructured particles, and physical vapor deposition for thin film deposition. The kinetics of the hydride thin films is characterized in a custom-built hermetic hydrogen optical cell. The surface topologies of the thin films are studied by atomic force microscopy. The optical phonons discussed in this thesis were mostly studied by Raman spectroscopy.
1.1 Organization of the Thesis

The remaining chapters of the thesis are arranged as follows:

**Chapter 2** consists of a literature review on the hydrogen storage materials, characterization techniques, and material preparation methods employed in this thesis. It also reviews hydride-based thin films and film growth mechanisms.

**Chapter 3** investigates the dehydrogenation characteristics of magnesium catalyzed by nickel and titanium in terms of kinetics and thermodynamics, based on volumetric techniques and differential scanning calorimetry.

**Chapter 4** demonstrates a simple and effective optical technique coupled with image processing to detect the onset temperature and monitor the kinetics of hydrogen release and absorption in real time for hydride materials in powder form, including magnesium nanowires, which were fabricated via physical vapor deposition in a transparent quartz tube.

**Chapter 5** investigates the kinetics of de/hydrogenation and the Raman vibrational spectra of magnesium thin film prepared by pulsed-laser deposition. Vibrational calculations in CASTEP are included for comparison.

**Chapter 6** presents and demonstrates the concept of a multi-stacked film structure that has the capability to significantly enhance the optical contrast of ultrathin film switchable mirrors, while preserving much of the rapid switching speed of ultrathin films. The ultimate aim is to create a superlattice structure.

Finally, **Chapter 7** draws conclusions for each chapter and presents a program for future work, including a proposal to fabricate a nano-stage setup to experimentally
investigate the properties of a single magnesium nanowire, the width of which is reduced to below 1 nm. I also discuss the possible release of hydrogen from hydrides by resonant photodesorption at room-temperature.

1.2 Contributions of thesis

Specifically, the main contributions of this thesis are as follows:

- Demonstration of the proof-of-principle that interaction between visible light and a magnesium hydride sample in reflective mode can be used to determine the desorption temperature and kinetics of magnesium hydride powder/nanowires fabricated inside a transparent quartz tube by the physical vapor deposition method.

- Calculation of the absorption and reflectance of magnesium and magnesium hydride due to electronic transitions.

- Fabrication of an 11 nm magnesium thin film capped with 2 nm palladium by the pulsed-laser deposition technique that could absorb and release hydrogen at room temperature within 5 minutes.

- Measurement of Raman vibrational spectra for the 11 nm magnesium hydride film.

• Proposal and demonstration of a multi-stacked structure intended for ultrathin films of hydrides that would boost the switching contrast to the equivalent of a “thicker” film and yet be able to retain much of the desirable fast switching speed associated with ultrathin film.

• Determination of the hydrogen diffusion pathway for the multi-stacked Pd-C₆₀-Pd structure.

• Fabrication of a series of single layer Pd thin films 2 nm, 5 nm, 10 nm, 17 nm, 23 nm, and 35 nm in thickness by vacuum evaporation with real-time thickness monitoring and control.

• Measurement of the absorption coefficient of the single layer Pd thin films.

• Measurement of the response and recovery times in a single temporal profile for the 2 nm Pd ultrathin film.

• Investigation of the dehydrogenation characteristics of magnesium catalyzed by titanium and Ni/Ti.

### 1.3 References


Chapter 2

Literature review

2.1 Background

Earth’s climate has been reasonably stable for the past 10000 years or so apart from the intermittent occurrence of the ice ages. This intricate equilibrium of the Earth's atmosphere began to be perturbed soon after the industrial revolution started. In past decades, efforts to harness renewable energy were driven mainly by idealism and concerns about energy security, and less so by concern for preserving or restoring the intricate balance of the Earth’s atmosphere. In recent years, however, as the adverse effects on the environment such as rising global temperature caused by the excessive burning of fossil fuels are becoming ever more pronounced, it has become ever more pressing to search for an alternative and sustainable energy carrier to meet our energy needs. Such urgency and efforts cannot be too strongly justified, as it is about preserving and restoring the health of the Earth’s biosphere of which we are a part, and one that has been supporting us, and will continue to do so for generations to come, provided that we restore the complex dynamical balance in time before the damage becomes irreversible.

The United Nations’ Intergovernmental Panel on Climate Change (IPCC) predicts widespread and drastic impacts on ecosystems, water resources, food and fiber production, coastlines, and human health if the global temperature continues to rise [1].
Dying forests in Europe and acid rain were among the wake-up calls to the need to regulate the levels of sulfur, nitrogen oxides, hydrofluorocarbons (HFCs), particulate emissions, and other pollutants. Numerous scientific studies on climate change have finally seemed to convince government agencies and law makers around the world that global warming is indeed a real problem and swift action is needed. As a consequence, “zero emissions” from cars, buses, and industry is gradually becoming the new world standard [1].

One solution to the global warming is to use renewable energy such as solar, wind and using hydrogen as an energy carrier. The concept of the “hydrogen economy” was coined by John Bockris during a talk he gave in 1970 at General Motors (GM) Technical Center [2]. Hydrogen advocates promote hydrogen as a potential energy carrier for motive power (such as in cars and boats), industry, and homes [3].

Hydrogen was first identified as a distinct chemical element by the British scientist Henry Cavendish in 1766 after he separated hydrogen gas by reacting zinc metal with hydrochloric acid. In a demonstration to the Royal Society of London, Cavendish applied a spark to hydrogen gas, yielding water. This discovery led to his later finding that a water molecule (H2O) consists of hydrogen and oxygen [4].

Hydrogen is used in many industries as a chemical raw material, such as in the production of fertilizer, dyes, and plastics. It is also used to hydrogenate oils and fats, to make gasoline from coal, and to produce methanol. Liquid hydrogen has been used as rocket fuel in combination with liquid oxygen [1].

The Soviet Union Tupolev Design Bureau successfully converted one of the three engines of a TU-154 commercial airliner [1,5] to run on liquid hydrogen, and the experimental aircraft was named the TU-155 (Fig 2.1). The maiden flight took off on
April 15, 1988 and lasted for 21 minutes [1,5]. Fig. 2.2 shows a schematic diagram of the hydrogen-powered TU-155. Note that the liquid hydrogen fuel tank in the rear of the fuselage.

![Experimental aircraft TU-155](image1.jpg)

Fig. 2.1 The experimental aircraft TU-155 with one of the engines running on liquid hydrogen (picture taken from Ref. 5).

![Schematic diagram of TU-155](image2.jpg)

Fig. 2.2 Schematic diagram of the TU-155 with a liquid hydrogen fuel tank (adapted from Ref. 1).
2.2 Physical properties of hydrogen

Hydrogen atom is the lightest element in the periodic table, and its most abundant isotope consists of only one proton and one electron. The hydrogen atoms (chemical symbol, H) readily form the hydrogen molecule \( \text{H}_2 \) in order to achieve a lower energy state.

\( \text{H}_2 \) molecules are smaller in size than most other molecules, and they are colorless, odorless, tasteless, and 14 times lighter than air. Hydrogen condenses to liquid at \(-253^\circ\text{C}\) and solidifies at \(-259^\circ\text{C}\). A more complete list of the physical properties of hydrogen is given in Table 2.1. Hydrogen gas has a density of around 0.09 kg m\(^{-3}\) and a buoyancy of 1.2 kg m\(^{-3}\) in air.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>2.01594</td>
</tr>
<tr>
<td>Density of gas at 0(^\circ)C and 1 atm.</td>
<td>0.08987 kg/m(^3)</td>
</tr>
<tr>
<td>Density of solid at (-259^\circ)C</td>
<td>858 kg/m(^3)</td>
</tr>
<tr>
<td>Density of liquid at (-253^\circ)C</td>
<td>708 kg/m(^3)</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>(-259^\circ)C</td>
</tr>
<tr>
<td>Boiling temperature at 1 atm.</td>
<td>(-253^\circ)C</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>(-240^\circ)C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>12.8 atm.</td>
</tr>
<tr>
<td>Critical density</td>
<td>31.2 kg/m(^3)</td>
</tr>
<tr>
<td>Heat of fusion at (-259^\circ)C</td>
<td>58 kJ/kg</td>
</tr>
<tr>
<td>Heat of vaporization at (-253^\circ)C</td>
<td>447 kJ/kg</td>
</tr>
<tr>
<td>Thermal conductivity at 25(^\circ)C</td>
<td>0.019 kJ/(ms(^{\circ})C)</td>
</tr>
<tr>
<td>Viscosity at 25(^\circ)C</td>
<td>0.00892 centipoise</td>
</tr>
<tr>
<td>Heat capacity ((C_p)) of gas at 25(^\circ)C</td>
<td>14.3 kJ/(kg(^{\circ})C)</td>
</tr>
<tr>
<td>Heat capacity ((C_p)) of liquid at (-256^\circ)C</td>
<td>8.1 kJ/(kg(^{\circ})C)</td>
</tr>
<tr>
<td>Heat capacity ((C_p)) of solid at (-259.8^\circ)C</td>
<td>2.63 kJ/(kg(^{\circ})C)</td>
</tr>
</tbody>
</table>
2.3 Chemical properties of hydrogen

Hydrogen gas is relatively non-reactive at room temperature unless it has been activated in some way, and for that reason, a temperature as high as 4700°C is needed to dissociate hydrogen molecules into hydrogen atoms [7]. The hydrogen atom, on the other hand, is very reactive, and for that reason, it does not exist freely in nature where hydrogen is often bound to either oxygen or carbon atoms. To obtain hydrogen from natural compounds, energy input is needed to isolate the hydrogen. For this reason, hydrogen should be regarded as an energy carrier.

The hydrogen atom is a strong reducing agent, and it can react with oxides and chlorides of many metals such as silver, copper and lead to produce the free metals [8]. It also reacts with numerous metallic and non-metallic elements to yield hydrides such as NH₃, NaH, and H₂S [6]. When hydrogen reacts with oxygen in a combustion or electrochemical conversion process to generate energy, the resulting reaction product is water vapor.

2.4 Fuel properties of hydrogen

Hydrogen is highly flammable over wide ranges of temperature and gas concentration. The reaction between hydrogen and oxygen releases energy in an explosive manner, as in a hydrogen-powered combustion engine, or generates electricity quietly in fuel cells to produce water as its only by-product [1].

Hydrogen has the highest energy content per unit mass of any fuel. On a mass basis (gravimetric), the energy density of liquid hydrogen (33.3 kWh kg⁻¹) is almost three times that of gasoline (12.7 kWh kg⁻¹). On a volume basis, however, liquid hydrogen has an energy density of only 2.4 kWh L⁻¹ compared with 8.7 kWh L⁻¹ for gasoline.
Table 2.2 shows the energy density comparison between hydrogen and other energy carriers such as liquefied petroleum gas (LPG) and methanol.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravitimetric energy density (kWh kg⁻¹)</td>
<td>33.3</td>
<td>33.3</td>
<td>13.9</td>
<td>5.6</td>
<td>12.9</td>
<td>12.7</td>
<td>0.03</td>
</tr>
<tr>
<td>Volumetric energy density (kWh L⁻¹)</td>
<td>0.53</td>
<td>2.4</td>
<td>2.6</td>
<td>4.4</td>
<td>7.5</td>
<td>8.7</td>
<td>0.09</td>
</tr>
</tbody>
</table>

An attractive feature of hydrogen is its electrochemical property, which enables hydrogen fuel cells to generate electricity. The currently available hydrogen-oxygen fuel cells are found to operate at an efficiency of 50 to 60% and with a lifetime of up to 3000 hours. Fig. 2.3(a) shows the Honda FCX Clarity, which is powered by hydrogen fuel. It has a 100 kW V-Flow fuel cell stack, a lithium-ion battery pack, a 95 kW electric motor, and a 340 atm compressed hydrogen gas storage tank that would yield a traveling distance of 434 km [10]. It was first rolled out for lease in 2008. Fig. 2.3(b) shows the hollow construction of the FCX Clarity electric motor with the drive-shaft passing through the center, which allows the motor and the gearbox to be integrated into a single unit [10]. Fig. 2.3(c) shows the onboard fuel cell stack used to convert the hydrogen supply into electricity to power the electric motor.

The engineering team at Boeing Research & Technology Europe (BR&TE) has also demonstrated a fuel cell powered aircraft using a Proton Exchange Membrane (PEM) fuel cell [11] as shown in Fig. 2.4. The airframe is a two-seater Dimona motor-glider with a 16.3 meter wingspan built by Diamond Aircraft Industries of Austria.
Apart from fuel cells, hydrogen can also be used in an internal combustion engine to generate traction torque. Before we go on further, it is instructive to look at the flammability of hydrogen, which is relevant to the combustion engine. Hydrogen gas is flammable under ambient conditions in a concentration of 4% to 75%, and is explosive in the 15% to 59% concentration range [12]. For application as fuel in an internal combustion engine, it is common to express the flammability range in terms of the equivalent ratio, $\varphi$, which is defined as the ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio [6]. The flammability range for hydrogen is $0.1 < \varphi < 7.1$, whereas the flammability range for gasoline is $0.7 < \varphi < 4$, and this suggests that the hydrogen-based internal combustion engine is more likely to be able to run smoothly even under highly dilute conditions [6]. The fuel economy is usually good because of complete combustion. A hydrogen powered car has a typical efficiency of around 45%, which is significantly higher than the 25% efficiency for a standard gasoline car. Furthermore, as the final combustion temperature is generally lower for engines running on hydrogen fuel than with gasoline, the resultant pollutants in the exhaust emission, such as nitrogen oxides, are reduced [6]. Researchers have also been exploring the concept of the multiple injection system, where hydrogen is injected directly into the cylinder once or twice within a combustion cycle to boost power density up to or exceeding that of the gasoline engine [13,14].

The BMW Hydrogen 7 is an example of a vehicle powered by a hydrogen-based internal combustion engine [15]. It features a bi-fuel internal combustion engine that can either run on hydrogen or gasoline [Fig. 2.5(a)]. The engine is based on the 12-cylinder V12 engine [Fig. 2.5(b)], as is used in BMW’s 7-series line of vehicles, and it has an acceleration from 0 to 96.6 km hour$^{-1}$ in 9.2 s. Unlike the Honda FCX Clarity,
the BMW Hydrogen 7 has a liquid hydrogen fuel tank. It has a traveling range of 201 km on hydrogen and over 482 km on gasoline [15].

Fig. 2.3 (a) The Honda FCX Clarity powered by compressed hydrogen [16]. (b) The hollow construction of the electric motor of the Clarity FCX, and (c) the onboard fuel cell used to convert compressed hydrogen into electricity [10].

Fig. 2.4 (a) A fuel cell electric-powered Dimona built by Boeing Research & Technology Europe [17]. Note the electric motor connected to the propeller. (b) The electric-powered Dimona motor-glider in flight [11].
2.5 Challenges to the hydrogen economy

It is clear from previous sections that the use of hydrogen as an energy carrier does have enormous benefits from an environmental perspective, and therefore, there has been intense research activity in the development of hydrogen-related technologies for the last 15 years [20]. A seemingly elegant and almost ideal concept it may be, but the realization of the hydrogen economy is, however, not without its challenges. There are three major technological obstacles that have been identified that are preventing the complete transition from the fossil fuel economy to the hydrogen economy within the next few decades [20], and they are the production of hydrogen gas, fuel cell development, and hydrogen storage systems.

2.5.1 Production of hydrogen gas

The first obstacle is the cost of production of hydrogen gas in a safe and efficient manner. Almost 50% of the supply of hydrogen is currently being produced from methane steam reforming, 30% from naphtha, 18% from coal gasification, and only

Fig. 2.5 (a) The BMW Hydrogen 7 [18]. (b) The bi-fuel V12 engine can run on either liquid hydrogen or gasoline [19].
3.9% from the electrolysis of water [21]. This means that the majority of the hydrogen available today is still derived from fossil fuels, and a study has suggested that the use of hydrogen which has been derived from fossil fuels as an energy carrier would actually produce more CO$_2$ than the direct use of the fossil fuels for power generation [22]. Fossil fuel-based processes are much cheaper than electrolysis of water, however, efforts are underway to reduce the cost of electrolysis-derived hydrogen to $2-3 per kg [20].

2.5.2 Fuel cell development

The second obstacle is associated with the development of the PEM fuel cell (PEMFC), which is the primary cell often considered as the cell most suitable for transportation. Efforts are still needed to extend the service life span, dynamics, and reliability of the cells [20,23]. The present cost of the energy derived from a PEMFC is about $200 per kW and it has to be reduced to a practical $30 per kW before the PEMFC can be commercialized on a full scale [20].

2.5.3 Hydrogen storage system

The third, and possibly the greatest, obstacle to the hydrogen economy is related to the search for suitable hydrogen storage systems to meet application demands. The suitable form of hydrogen storage is, nevertheless, application-specific. For instance, applications in the transportation sector require storage at a volume that can be accommodated within the confines of the vehicle and at a weight that does not adversely affect the performance of the vehicle. As for stationary applications, hydrogen storage designed for building-integrated applications is expected to have suitable volumetric storage density, while storages at power plants or remote locations will obviously have
less stringent energy storage density requirements, both in terms of volume and weight aspects. Given the fact that mobile applications in transportation poses the greatest challenge to the success of the hydrogen economy and account for more than half of the total national energy demands in developed countries such as the US [6,23], it is not surprising that much of the research effort on hydrogen storage has been focused on the research and development of hydrogen storage systems for transportation use that, besides the environmental benefits, will result in performance and a driving experience that are either on par or exceed that of vehicles currently powered by hydrocarbons. The next two sections will review the targets for onboard hydrogen storage for mobile applications and the available hydrogen storage options along with their shortcomings.

2.6 Targets for onboard hydrogen storage

Transportation in developed nations, such as the US, relies heavily on petroleum, and the usage demands account for more than two-third of all the oil used in the nation [24]. The challenges to migrate to electric or hydrogen powered vehicles are very daunting because gasoline-fueled (and diesel-fueled) vehicles powered by internal combustion engines (ICEs) have been invented for more than 100 years, and there is vast and well established supporting infrastructure, ranging from refueling, to maintenance and servicing.

In the United States, the Hydrogen Fuel Initiative was launched in 2003 with a funding of $1.2 billion over 5 years to accelerate the research, development, and demonstration of hydrogen and fuel-cell technologies.
The US Department of Energy (DOE) in collaboration with FreedomCAR, the Fuel Partnership, the US Council for automotive Research (USCAR), and other major energy companies has developed a comprehensive set of hydrogen storage system performance targets that would help to guide the long-term research and development of fuel cell vehicles (FCVs) [2]. It was established that onboard hydrogen storage in the range of approximately 5 to 13 kg is required to enable a driving range of greater than 482.8 km (300 miles) for light-duty automotive vehicles using fuel cell power plants [2], in order to successfully introduce them to the masses in an established automobile market dominated by gasoline-powered vehicles.

Among the two primary parameters of the DOE targets are the system gravimetric capacity and the system volumetric capacity. The system capacity is a measure of the energy density by considering the total onboard storage system. The onboard storage system should include components such as the tank, storage media, safety system, valves, regulators, piping, mounting brackets, and insulation. Obviously, the gravimetric and volumetric capacities of the storage media alone must be higher than the system-level targets [2]. Note also that the targets developed are customer-driven, which was designed to achieve similar performance and cost levels to competitive vehicles. Table 2.3 shows some of the quantitative targets established in 2003 for FCV onboard storage systems.

The hydrogen storage system targets are reviewed every five years to assess technological improvements and to ensure continued alignment with market driven requirements. In 2009, the Onboard Hydrogen Storage System targets were revised to reflect the knowledge gained on hydrogen-fuelled vehicles since the original release of the targets in 2003, and some of the important specifications are listed in Table 2.4 along with the old targets for comparison purposes.
Notably, the new 2015 targets for hydrogen energy densities are:

**System gravimetric capacity:** 1.8 kWh kg\(^{-1}\), or 5.5 wt% hydrogen

**System volumetric capacity:** 1.3 kWh L\(^{-1}\), or 0.040 kg hydrogen L\(^{-1}\)

The technical targets for transportation developed by the DOE inevitably pose great challenges for scientists and engineers to achieve because of vehicular constraints. The key challenges can be categorized into the following: 1) weight and volume, 2) efficiency, 3) durability, 4) hydrogen charging/discharging rates, 5) cost, and 6) environmental, safety, and health considerations.

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System gravimetric capacity.</strong> Usable, specific energy from ( \text{H}_2 ) (not useful energy/ max system mass)(^a)</td>
<td>kWh/kg (kg ( \text{H}_2 )/kg system)</td>
<td>2 (0.06)</td>
<td>3 (0.09)</td>
</tr>
<tr>
<td><strong>System volumetric capacity.</strong> Usable energy density from ( \text{H}_2 ) (not useful energy/ max system volume)(^b)</td>
<td>kWh/L (kg ( \text{H}_2 )/L system)</td>
<td>1.5 (0.045)</td>
<td>2.7 (0.081)</td>
</tr>
<tr>
<td><strong>Storage system cost</strong>(^b) (and fuel cost)(^c)</td>
<td>$/kWh net ($/kg ( \text{H}_2 ))</td>
<td>4 (133)</td>
<td>2 (67)</td>
</tr>
<tr>
<td></td>
<td>$/gpm at pump</td>
<td>2–3</td>
<td>2–3</td>
</tr>
<tr>
<td><strong>Durability/operability</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating ambient temperature(^d)</td>
<td>°C</td>
<td>−30/50 (sun)</td>
<td>−40/60 (sun)</td>
</tr>
<tr>
<td>Minimum/maximum delivery temperature</td>
<td>°C</td>
<td>−40/85</td>
<td>−40/85</td>
</tr>
<tr>
<td>Cycle life (one-fourth tank to full)(^e)</td>
<td>Cycles</td>
<td>1000</td>
<td>1500</td>
</tr>
<tr>
<td>Cycle life variation(^f)</td>
<td>% of mean (min) at % confidence</td>
<td>90/90</td>
<td>90/90</td>
</tr>
<tr>
<td>Minimum delivery pressure from storage system; FC = fuel cell, ICE = internal combustion engine</td>
<td>atm (absolute)</td>
<td>4FC/35 ICE</td>
<td>3FC/35 ICE</td>
</tr>
<tr>
<td>Maximum delivery pressure from storage system(^g)</td>
<td>atm (absolute)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>Charging/discharging rates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System fill time (for 5 kg)</td>
<td>min</td>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>Minimum full-flow rate</td>
<td>(g/s)/kW</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Start time to full flow (20°C)(^h)</td>
<td>s</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Start time to full flow (−20°C)(^h)</td>
<td>s</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Transient response 10%–90% and 90%–0%(^i)</td>
<td>s</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Fuel purity (( \text{H}_2 ) from storage)</td>
<td>% ( \text{H}_2 )</td>
<td>99.99 (Dry basis)</td>
<td></td>
</tr>
<tr>
<td>Environmental, health, and safety</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permeation and leakage(^j)</td>
<td>SCC/h</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Toxicity</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Safety</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Loss of usable ( \text{H}_2 )(^l)</td>
<td>(g/h)/kg ( \text{H}_2 ) stored</td>
<td>0.1</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Table 2.4 The new US DOE Onboard Hydrogen Storage System targets revised in 2009 for light-duty vehicles [2]. The old targets are included for comparison.

<table>
<thead>
<tr>
<th>Target</th>
<th>2010 (new)</th>
<th>2010 (old)</th>
<th>2015 (new)</th>
<th>2015 (old)</th>
<th>Ultimate Full Fleet</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Density (% wt)</td>
<td>4.5 (1.5 kWh/kg)</td>
<td>6 (2.0 kWh/kg)</td>
<td>5.5 (1.8 kWh/kg)</td>
<td>9 (3 kWh/kg)</td>
<td>7.5 (2.5 kWh/kg)</td>
</tr>
<tr>
<td>System Volumetric Density (g/L)</td>
<td>28 (0.9 kWh/L)</td>
<td>45 (1.5 kWh/L)</td>
<td>40 (1.3 kWh/L)</td>
<td>81 (2.7 kWh/L)</td>
<td>70 (2.3 kWh/L)</td>
</tr>
<tr>
<td>System Fill Time for 5-kg fill, min (Fueling Rate, kg/min)</td>
<td>4.2 min (1.2 kg/min)</td>
<td>3 min (1.67 kg/min)</td>
<td>3.3 min (1.5 kg/min)</td>
<td>2.5 min (2.0 kg/min)</td>
<td>2.5 min (2.0 kg/min)</td>
</tr>
<tr>
<td>Storage System Cost ($/kg H₂): To be determined in conjunction with other Partnership cost target changes</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
</tbody>
</table>

2.7 Potential technologies available for hydrogen

In this section the technologies available for hydrogen storage are reviewed in general. The technologies that are being considered for hydrogen storage are compressed hydrogen, cryogenic hydrogen, metal hydrides, high-surface-area adsorbents, and chemical hydrogen storage materials [2]. Among these technologies, the compressed hydrogen and the cryogenic hydrogen are considered mature technology. In fact, compressed hydrogen has been used in demonstration vehicles for many years, and most prototype hydrogen vehicles use this type of storage [25].

A significant challenge of hydrogen storage for transportation applications is the limited physical space available within a vehicle. So despite being a mature technology, compressed hydrogen with a pressure of 70-80 MPa (i.e. about 800 atm, or 800 kg cm⁻¹, which is almost equivalent to the weight of a small car impinging on a one cm² area!) only gives a resultant energy density of 1.2 kWh L⁻¹, which is still much lower than that of gasoline at 8.7 kWh L⁻¹ [20,26]. Furthermore, the 80 MPa pressure in the hydrogen gas cylinders also raises safety concerns, particularly in the event of an accident. There
is also cost and energy consumption associated with the high pressure compression process. Finally, there is concern about hydrogen embrittlement in metal because the majority of the internal metallic parts of the system are exposed to high pressure hydrogen for a long period of time [20].

Liquid hydrogen is stored in cryogenic tanks at -295°C at ambient pressure. The main disadvantages of liquid hydrogen as an energy carrier are the boil-off of hydrogen over time, the large amount of energy required for hydrogen liquefaction, and the safety concerns relating to cryogenic fluid in the event of accident. The rate of hydrogen boil-off mainly depends on the effectiveness of the thermal insulation, ambient conditions, geometry of the vessel, and length of time between driving [27]. For example, the BMW Hydrogen 7 mentioned earlier in this thesis will boil off all of its liquid hydrogen in less than 2 weeks [6]. The liquid hydrogen has a significantly lower total fuel cycle energy efficiency than gaseous hydrogen because of the large amount of energy required for liquefaction [28,29]. The total theoretical amount of energy required for liquefaction is approximately 0.94 kWh kg⁻¹, whereas the actual amount of energy required for liquefaction is much higher, approximately 14 kWh kg⁻¹, with a refrigeration efficiency of 7.2% [30]. Overall, the liquefaction results in a loss of about 30% of the energy stored in liquid hydrogen.

High-surface-area adsorbent storage relies on the physisorption of molecular hydrogen on materials with a large specific surface area, such as Metal Organic Frameworks (MOFs) and carbon materials [31,32]. The high-surface-area adsorbents have a fully reversible hydrogen uptake-and-release behavior, since the storage mechanism is based on physisorption, and there are no large activation barriers to be overcome during dehydrogenation [33]. The hydrogen storage capacity of MOFs at -195°C has been
reported to be as high as 4 wt%, with a room temperature capacity of approximately 1 wt%. However, the volumetric hydrogen capacity is still a significant issue due to the highly porous nature of these materials [34].

The use of carbon nanotubes for hydrogen storage via physisorption has previously attracted attention, however, contrary to intuition, it is now clear that the nanotubes do not store hydrogen gas in their voids but only as an adsorbent to the side walls, which means that the storage capacity is no greater than that of any other carbon surface [35].

The DOE Hydrogen Program has, in fact, determined that maximum hydrogen capacity of single-walled carbon nanotubes to be 0.6 wt% at room temperature, and 3 wt% at 77 K, respectively [36]. As the single-walled carbon nanotubes do not meet the target requirement of 6 wt% hydrogen storage at room temperature on a materials basis, the DOE Hydrogen Program decided on a “No-Go” decision for future investment in applied research and development (R&D) in single walled carbon nanotubes for vehicular hydrogen storage applications in 2006 [37]. However, there are certain areas of carbon nanotube research, such as metal-doped hybrid materials, that may still be worth research effort.

Chemical hydrogen storage materials release hydrogen on demand when reacted with water, although they are likely to be non-reversible and have to be recycled off-board. The amount of water needed to be carried onboard will reduce the effective gravimetric energy density of the system. The major challenge of this storage method is the reversibility and the control of the thermal reduction process in order to produce the metal in a solar furnace. The process has been successfully demonstrated with zinc [38].

Based on the available options mentioned above, the US DOE has determined that hydrogen storage via solid metal hydrides is the most viable option to, at least partially,
meet the stringent target requirements for onboard hydrogen storage on a long-term basis, and thus the remaining part of this chapter will focus on a review of the various solid metal hydrides.

2.8 Brief history of metal-hydrides

Hydrogen has been used for energy generation since the 1800s, and in 1802, Sir William Grove built a gaseous voltaic battery, considered as the first hydrogen fuel cell [20]. In 1866, Graham observed the ability of palladium to absorb hydrogen gas, and the reversible absorption was further observed to proceed in the presence of either pure palladium or palladium-silver alloys. The reaction of hydrogen with palladium was historically described by Graham as $\text{Pd} + \text{H}_2 \leftrightarrow \text{PdH}_x$. Palladium hydride is non-stoichiometric chemical compound. Furthermore, hydrogen is dissolved and stored in spaces between the Pd atoms of the crystal lattice, which is analogous to a conventional sponge soaking up water.

Since the discovery of palladium hydride, other metal-hydrogen systems have been investigated in metals, such as Ni, Fe, Co, Cu, Pd, Pt, Rh, Ag-Cu, Cu-Ni, Cu-Pt and Cu-Sn [20,39–42]. Among the metals found to absorb hydrogen were Ag, Au, Cd, Pb, Sn, and Zn. Around the same time that Sieverts et al. first reported studies on absorption of hydrogen by metals and alloys, Avrami [43–45] reported on his findings on the kinetics of phase transformations driven by nucleation and growth of nuclei, which forms part of the foundations for hydrogen storage and our understanding of microstructures in solid materials.
After the second world war, liquid hydrogen was intensively researched as rocket fuel, and investigation of hydrides was driven mainly by nuclear reactor applications where there was a need to understand the hydride-caused embrittlement of reactor metals, such as Zr. The first intermetallic hydride reported was the ZrNiH$_3$ [46]. By the end of the 1960s many metals were found to have the ability to form hydrides, albeit some of them were found to be too stable for reversible hydrogen sorption, such as ZrH$_2$, or too unstable, such as NiH [20].

2.9 Properties of hydrides and characterization

We here briefly discuss the essential properties of hydrides and their characterization techniques.

2.9.1 Thermodynamics of hydrides

The thermodynamical properties of solid hydrides such as the enthalpy and entropy can be determined from the so-called pressure-composition-isotherm (PCI) curve, which is also known as the pressure-composition-temperature (PCT) curve. It is essentially a plot of the logarithm of the hydrogen equilibrium pressure versus the hydrogen gravimetric capacity of the metal-hydride sample. There are several methods of determining PCI properties, ranging from thermogravimetric analysis to precise volumetric measurements obtained by using a classical Sieverts-type apparatus. The thermogravimetric methods are extremely limited in pressure.

A typical isotherm of a reversible metal-hydride acquired using the volumetric method is shown in Fig. 2.6(a). By measuring the changes in hydrogen pressure and the
corresponding changes in the hydrogen concentration in metal at a given temperature (e.g. \( T_1 \)), a PCT curve can be constructed. The signature of a PCT curve is the flat plateau observed while the material is undergoing hydride phase transformation. Most practical hydrides, however, do not show a perfectly flat plateau or zero hysteresis. Sloping behavior is observed, possibly due to different equilibrium pressure, localized defects, and surface inhomogenities [47].

![Fig. 2.6 (a) Pressure-composition-isotherm (PCI) curves at temperatures \( T_1 \), \( T_2 \), and \( T_3 \). (b) The corresponding van’t Hoff plot constructed based on the PCI curves.](image)

It can be seen in Fig. 2.6(a) that as the temperature increases from \( T_1 \) to \( T_2 \), the corresponding plateau pressure increases as well. Also note that as the temperature increases from \( T_1 \) to \( T_3 \), the length of the plateau becomes progressively shorter. The length of plateau determines the amount of hydrogen that can be stored reversibly at a given temperature.

Now let’s look a bit closer at the hydrogen absorption process itself, assuming that the hydride we are looking at is an interstitial hydride, that is, a metal which acts like a hydrogen sponge. One example of such a metal is palladium. A small amount of hydrogen is initially dissolved in the metal (i.e., with the hydrogen to metal ratio, \( H/M < \))
0.1) and creates a solid solution of hydrogen within the host metal. In this case, the phase is known as the $\alpha$-phase. The metal lattice expands proportionally to the hydrogen concentration by about 2 to 3 Å$^3$ per hydrogen atom [48]. If there is a greater hydrogen concentration in the host metal ($H/M > 0.1$), a strong hydrogen-hydrogen interaction becomes significant because of the lattice expansion, and the hydride phase nucleates and grows. This hydride phase is called the $\beta$-phase, and the hydrogen concentration is often found to be $H/M = 1$ [49]. In the plateau region, there exists a mixture of solid solution $\alpha$-phase and the metal hydride $\beta$-phase. Above the critical temperature ($T_c$), the plateau region disappears and the $\alpha$-phase converts to the $\beta$-phase continuously [20].

The relation between the midplateau equilibrium pressure $P_{eq}$ and the isothermal temperature $T$ of the sample is given by the well known van’t Hoff equation [20]:

$$\ln\left(\frac{P_{eq}}{P}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

(2.1)

where $P$ is the atmospheric pressure (1 atm), $\Delta H$ and $\Delta S$ are the enthalpy and entropy changes of the hydriding/dehydriding reaction, respectively and $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$). For almost all hydrides (with a few exceptions) the enthalpy and entropy of hydriding reaction are negative, i.e., the hydriding reaction is exothermic and dehydriding reaction is endothermic. Unless otherwise stated, both the $\Delta H$ and the $\Delta S$ are expressed as per 1 mol H$_2$ in this thesis.

As the entropy change corresponds mostly to the change from molecular hydrogen gas to dissociate into hydrogen atoms, it is approximately the standard entropy of hydrogen and therefore, $|\Delta S| \approx 130$ J·K$^{-1}$·mol$^{-1}$H$_2$ for all metal-hydrogen systems [20].
The $\Delta H$ term characterizes the stability of the metal hydrogen bond. To reach an equilibrium pressure of 1 bar at 300 K, $\Delta H$ should be 39.2 kJ mol$^{-1}$ H$_2$ [20,49]. The entropy of formation term for metal hydrides leads to a significant heat evolution, $\Delta Q = T \cdot \Delta S$ (exothermic reaction) during the hydrogen absorption process. The same amount of heat has to be provided to the metal hydride to desorb the hydrogen (endothermic reaction). If the hydrogen desorption occurs below room temperature, then the required heat can be supplied by the environment. However, if the desorption takes place above room temperature, then the required heat has to be supplied by an external source. The external heat can also come from the combustion of hydrogen. For a stable hydride such as magnesium hydride (MgH$_2$), the heat required for the desorption of hydrogen at 300°C and 1 bar is $\approx$ 25% of the heating value of hydrogen [50].

A plot of the logarithmic of the midplateau pressure against the reciprocal temperature, $\ln P_{eq}$ vs. $1/T$ is known as the van’t Hoff plot, and the enthalpy of absorption and desorption processes, $\Delta H$, can be determined from the linear slope ($-\Delta H/R$), as shown in Fig. 2.6(b). The operating temperature of the metal hydride depends on the plateau pressure and on the overall reaction kinetics. Higher temperature will results in faster kinetics.

The hydrogen capacity, $H_{cap}$ in Fig. 2.6(a) can be expressed in either the hydrogen to metal ratio, H/M, or the mass percent (wt%) [51]. In the mass percent calculation, both the mass of the hydrogen $m_h$ and the mass of the metal $m_M$ are considered in the denominator:

\[
H_{cap} = \frac{m_h}{m_{H,\text{hydride}}} \text{[wt%]} \tag{2.2}
\]
where mass of hydride, \( m_{\text{Hydride}} = m_{\text{metal}} + m_{\text{H}} \).

Capacity presentation in wt\% is very useful because it gives direct information on the amount of hydrogen that can be stored in a material.

If we substitute \( P = 1 \) atm into the van’t Hoff equation [Eq. (2.1)], we find that it reduces to [20]

\[
\Delta H = \Delta S \cdot T
\]  

Eq. 2.3 implies that we can determine the de/absorption temperature of a hydride at 1 atm, once the \( \Delta H \) and \( \Delta S \) are known.

Eq. 2.3 has been plotted for a number of hydrides, as shown in Fig. 2.7 [52]. Also note that most of the data points are fit well by a straight line. The gradient of the plot corresponds to the value of \( \Delta S \) and is indeed approximately equals to -130 J·mol\(^{-1}\)K\(^{-1}\) [52]. Figure 2.7 also shows that a low desorption temperature at 1 atm of pressure (more or less the operating pressure of a PEM fuel cell) can only be achieved with hydrides having hydrogenation/ desorption enthalpies no larger than 50 kJ·mol\(^{-1}\). For example, hydrides that desorb at room temperature, such as LaNi\(_5\) and TiFe, have \( \Delta H \) of about 30 and 33.3 kJ·mol\(^{-1}\), respectively [53]. However, if the enthalpy is too low, it would require \( T \) at 1 atm to be much lower than 0°C. From this point of view, the enthalpy term is one of the most important factors characterizing any hydride to be used as hydrogen storage.
Fig. 2.7 Hydride formation enthalpy, $\Delta H$, as a function of the isothermal temperature, $T$, at 1 atm. The isothermal temperature was calculated from thermodynamical parameters using the van’t Hoff equation [52].

2.9.2 Kinetics of hydrides

The thermodynamics covered in the previous section allows us to determine the temperature at which hydrogen absorption/desorption occurs, but it does not give us any information about the rate at which these processes take place. The study of the rate of hydrogen absorption/desorption of hydrides is known as chemical kinetics.

2.9.2.1 Free energy

To understand kinetics, it is helpful to invoke the concept of free energy. Fig. 2.8 shows the free energy curve for a single atom undergoing a chemical reaction. The initial state is the state before the atom undergoes the chemical reaction, and the final stage is when the atom has undergone the chemical reaction. If $G_i$ and $G_f$ are the free energies of the initial and final states, then the driving force for the transformation will be $\Delta G = G_f - G_i$. Before the free energy of the atom can be reduced from $G_i$ to $G_f$, the
atom must overcome a positive energy barrier greater than \( G_1 \), which is commonly known as the activation energy, \( E_A \).

A piece of bulk hydride material obviously consists of a large number of atoms, and above 0 K, at any given time, there is a finite probability that a particular atom may have enough thermal energy to overcome the energy barrier/activation energy. The collective random process that allows an atom within the bulk material to overcome the energy barrier to reach the state of lower free energy is known as the thermal activation [54].

![Free energy curve](image)

Fig. 2.8 Free energy curve showing the transformation from initial to final state through an activation energy barrier, \( E_A \) (adapted from Ref. 20).

**2.9.2.2 Calculation of activation energy using the Kissinger equation**

A common method used to calculate the activation energy is the Kissinger method, which is based on differential scanning calorimetry (DSC) of decomposition or formation processes and the endo- or exothermic peak positions which are related to these reactions and dependent on the rate of heating of the sample material [55]. The
mathematical expression that relates the temperature of the peak maximum \( T_{\text{max}} \), the heating rate \( \beta \), and the activation energy \( E_A \) is known as the Kissinger equation

\[
\ln(\beta / T_{\text{max}}^2) = -\frac{E_A}{RT_{\text{max}}}
\]  

(2.4)

The activation energy \( E_A \) can therefore be determined from the gradient of the linear plot of \( \ln(\beta / T_{\text{max}}^2) \) vs. \( T_{\text{max}} \).

### 2.9.3 Sorption measurements

Hydrogen gas sorption characterization is central to the study of hydrides for hydrogen storage materials. It provides critical information about the hydrogen sorption behavior of hydrogen storage materials in such aspects as hydrogen capacity, cycling performance of reversible materials, the rate of hydrogen de/absorption (kinetics), and the thermodynamic properties of the material, such as are revealed by the pressure-composition-isotherm (PCI) curves. The PCI curves would then allow the entropy and enthalpy of hydrogen de/absorption of the given material to be calculated, and hence, the temperature of hydrogen de/absorption at a given ambient pressure.

Several techniques are used for hydrogen sorption measurements, and the most common are the gravimetric (by detecting change in mass) and the volumetric (by detecting change in volume) methods. In the volumetric approach, the amount of hydrogen gas de/absorbed is usually determined by monitoring a change in the gas pressure within a calibrated volume containing the hydrogen storage sample.

The volumetric approach tends to be the preferred technique because the gravimetric method is susceptible to buoyancy [56] if the gas pressure and temperature change
significantly, and this could cause the calculated amount of hydrogen sorption from the sample to be misinterpreted if the buoyancy is not properly taken into account [57].

One of the most common configurations of the volumetric method is one based on Sieverts’ Apparatus. Sieverts’ Apparatus is basically a setup which consists of two gas chambers of known volume connected to each other by an isolation valve [58,59]. The amount of hydrogen absorption or desorption can be determine by the application of the Ideal Gas Law [20]:

\[ PV = nRT \]  \hspace{1cm} (2.5)

where

- \( P \): gas pressure;
- \( V \): gas volume;
- \( n \): number of moles of gas;
- \( T \): absolute temperature;
- \( R \): universal gas constant.

Eq. 2.5 states that for a constant volume and temperature, the gas pressure is proportional to the number of moles of hydrogen gas, \( n \).

If the hydrogen pressure is \( P_1 \), the number of moles of hydrogen is \( n_1 \), and the temperature is \( T \), then the Ideal gas Law becomes

\[ P_1V = n_1RT \]  \hspace{1cm} (2.6)

Once the hydrogen pressure has reached equilibrium after hydrogen desorption or absorption, Eq. 2.6 then becomes

\[ P_2V = n_2RT \]  \hspace{1cm} (2.7)

where \( P_1 > P_2 \) for hydrogen absorption, and \( P_1 < P_2 \) for desorption.
Both Eq. 2.6 and Eq. 2.7 can be rewritten as

\[ n_1 = \frac{PV}{RT} ; \quad n_2 = \frac{PV}{RT} \]  

(2.8)

From which, the difference between the number of moles of hydrogen in the system resulting from absorption or desorption is

\[ \Delta n = n_1 - n_2 = \Delta P \frac{V}{RT} \]  

(2.9)

where \( \Delta P = P_1 - P_2 \)

The mass of absorbed or desorbed hydrogen can be calculated using the number of moles of gas and molecular mass of hydrogen: \( m_{ii} = 2.016\Delta n \), which combined with Eq. 2.9 will give us:

\[ m_{ii} = 2.016\Delta P \frac{V}{RT} \]  

(2.10)

When the change in the hydrogen mass due to hydrogen de/absorption has been calculated using Eq. 2.10, we can then determine the hydrogen capacity of the sample material based on Eq. 2.2.

The ideal gas law should be replaced by the more elaborate but more accurate van der Waals equation for characterization involving hydrogen gas pressures higher than 50 atm [20].

\[ \left( P + \frac{n^2a}{V^2} \right)(V - nb) = nRT \]  

(2.11)
where $a$ is a measure of the attraction between hydrogen particles ($0.2476 \text{ L}^2 \text{ bar mol}^{-2}$) and $b$ is the volume excluded by one mole of hydrogen particles ($0.02661 \text{ L mol}^{-1}$).

### 2.10 Hydrogen storage in metal-hydrides

Hydrogen reacts at elevated temperatures with many transition metals and their alloys to form hydrides. The electropositive elements are the most reactive, i.e. Sc, Yt, lanthanides, actinides, and members of the Ti and V groups [49].

To be considered as a suitable candidate for onboard hydrogen storage for vehicular applications (assuming that the vehicles are powered by PEM fuel cells), a metal hydride should have the following properties based on the DOE 2009 revised targets [2]:

- High hydrogen capacity per unit mass and unit volume (> 5.5 wt% hydrogen, and > 40 g hydrogen L$^{-1}$, respectively, on the basis of the hydride material itself)
- Capable of operating within the operation pressure-temperature window of the PEM fuel cell, i.e. pressure: 1 to 10 atm, and temperature: 25 to 120°C
- Low heat of formation to minimize the energy necessary for hydrogen release and low heat dissipation during the exothermic hydride formation
- Reversibility for limited energy loss during charge and discharge of hydrogen
- Fast kinetics
- Good cycling stability
- Low cost of recycling and charging infrastructure
- High safety
There are over 50 metallic elements on the periodic table that can absorb a large amount of hydrogen, and so the possible choices of hydride materials are seemingly enormous. However, there are only a handful of them which are capable of hydrogen storage at moderate temperatures and pressures, and the choices are narrowed down even further if we impose the characteristic requirements set out by the US DOE. To tailor metal-hydride properties to meet the requirements, metallic alloys of various compositions are being investigated. These alloys can be classified as \( \text{AB}_5 \) (e.g., \( \text{LaNi}_5 \)), \( \text{AB} \) (e.g., \( \text{FeTi} \)), \( \text{A}_2\text{B} \) (e.g., \( \text{Mg}_2\text{Ni} \)), and \( \text{AB}_2 \) (e.g., \( \text{ZrV}_2 \)) [49].

Fig. 2.9 shows the comparison of volumetric and gravimetric hydrogen storage densities for different metal hydrides along with compressed hydrogen, liquid hydrogen, and carbon materials. Metals and their alloys can often store hydrogen at volume densities more than twice that of liquid hydrogen [60] as evidenced from Fig. 2.9. On the gravimetric capacity basis however, the local hydrogen capacities of these hydrides are often 10 wt% or less. \( \text{Mg}_2\text{FeH}_6 \) has the highest known volumetric density of 150 kg·m\(^{-3}\), which is more than double that of liquid hydrogen. \( \text{BaReH}_9 \) has the largest H/M ratio of 4.5 (i.e. 4.5 hydrogen atoms per metal atom). \( \text{LiBH}_4 \) shows the highest theoretical gravimetric hydrogen density of 18 wt% [50,60].
2.10.1 Model for hydride formation and dissociation

The first step in the formation of metal hydrides and solid solutions from molecular hydrogen occurs on the surface of the host metal. The first attractive force experienced by the hydrogen molecule as it approaches the metal surface is the van der Waals force which has a physisorbed state of energy of about 5 kJ mol\(^{-1}\) \(\text{H}\) at a distance of about 1 hydrogen molecule radius (~ 0.2 nm) from the metal surface [50]. Closer to the surface, the hydrogen molecule has to overcome an activation energy barrier for dissociation and formation of the hydrogen metal bond. The height of the activation barrier depends on the surface elements involved. Hydrogen atoms sharing their electron with the metal atoms at the surface are called chemisorbed [61]. The chemisorbed single H atoms may have high surface mobility. The H-metal bonding is electronic in nature, both in the bulk and at the surface [62]. However, the interaction of hydrogen with the electronic structure of the host metal in some binary hydrides and especially in the ternary hydrides is often more complicated. In many cases, the crystal structure of the host...
metal and thus the electronic structure change with the phase transition, and the theoretical calculation of the stability of the hydride becomes very complicated, if not impossible [50].

### 2.10.2 Binary and intermetallic hydrides

Metals, intermetallic compounds, and alloys generally react with hydrogen and form metal-hydrogen compounds. Hydrides exist in ionic, polymeric covalent, volatile covalent, and metallic forms as highlighted in various colors in Fig. 2.10. The difference between the various types of hydrides is not sharp, and they overlap into each other depending on the electronegativities of the elements. The electropositive elements such as scandium, yttrium, and the lanthanides are the most reactive [50].

![Fig. 2.10 Various class of hydrides highlighted in different colors [50].](image-url)
The binary hydrides, or metallic hydrides as they are usually referred to, are found to have metallic characteristics such as good electrical conductivity [50]. The metallic hydrides (MH\textsubscript{n}) often exhibit deviations from ideal stoichiometry [50]. In other words, the value of n is often a non-integer for metallic hydrides, such as n equals about 0.7, as in palladium hydride (PdH\textsubscript{0.7}). Metallic hydrides have a volumetric hydrogen density of around 115 kg\textperiodcentered m\textsuperscript{3} [50].

The lattice structure of binary hydrides is that of a typical metal with atoms of hydrogen occupying the interstitial sites and hence they are also known as interstitial hydrides. The hydrogen has a partial negative charge, depending on the type of host metal [63]. Only a few transition metals that do not form stable hydrides. Among them are nickel, chromium and copper [50]. Some of them, such as nickel and palladium are very effective in dissociating hydrogen molecules and they are therefore good catalysts for hydrogenation [50].

Table 2.5 shows some well known families of hydrides of the intermetallic compounds (A\textsubscript{x}B\textsubscript{y}) [64]. The A element is usually a rare earth or an alkaline earth metal that has the tendency to form stable hydride (high affinity to hydrogen). The B element, on the other hand, is often a transition metal and forms unstable hydrides (low affinity to hydrogen). The intermetallic compounds are classified according to their crystal structures, such as AB\textsubscript{2} type (Laves phase), AB\textsubscript{5} type (Haucke phase), and Ti-based body centered cubic (BCC) [65]. A distinctive feature of the intermetallic hydrides is their high volumetric hydrogen density. The highest volumetric hydrogen density known today is 150 kg\textperiodcentered m\textsuperscript{3} found in Mg\textsubscript{2}FeH\textsubscript{6} [66] and Al(BH\textsubscript{4})\textsubscript{3} [67], which exceed the 2015 target (Fig. 2.9). The properties of the intermetallic compounds can be tuned to some extend by varying their compositions. However, the low gravimetric hydrogen densities of intermetallic
hydrides limit their widespread use in mobile applications. For example, the LaNi$_5$ which can absorb and release hydrogen at room temperature at an acceptable rate has a gravimetric hydrogen density of only 1.5 wt%, which is far below the 2015 target (Table 2.4).

Table 2.5 The most important families of hydride-forming intermetallic hydride compounds [64].

<table>
<thead>
<tr>
<th>Intermetallic compound</th>
<th>Prototype</th>
<th>Hydrides</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB$_5$</td>
<td>LaNi$_5$</td>
<td>LaNi$_5$H$_6$</td>
<td>Haucke phases, hexagonal</td>
</tr>
<tr>
<td>AB$_2$</td>
<td>ZrV$_2$, ZrMn$_2$, TiMn$_2$</td>
<td>ZrV$<em>2$H$</em>{5.5}$</td>
<td>Laves phase, hexagonal or cubic</td>
</tr>
<tr>
<td>AB$_3$</td>
<td>CeNi$_3$, YFe$_3$</td>
<td>CeNi$_3$H$_4$</td>
<td>Hexagonal, PuNi$_3$-type</td>
</tr>
<tr>
<td>A$_2$B$_7$</td>
<td>Y$_2$Ni$_7$, Th$_2$Fe$_7$</td>
<td>Y$_2$Ni$_7$H$_3$</td>
<td>Hexagonal, Ce$_2$Ni$_7$-type</td>
</tr>
<tr>
<td>A$<em>6$B$</em>{23}$</td>
<td>Y$<em>6$Fe$</em>{23}$</td>
<td>Ho$<em>6$Fe$</em>{23}$H$_{12}$</td>
<td>Cubic, Th$<em>6$Mn$</em>{23}$-type</td>
</tr>
<tr>
<td>AB</td>
<td>TiFe, ZrNi</td>
<td>TiFeH$_2$</td>
<td>Cubic, CsCl-/CrB-type</td>
</tr>
<tr>
<td>A$_3$B</td>
<td>Mg$_2$Ni, Ti$_2$Ni</td>
<td>Mg$_2$NiH$_4$</td>
<td>Cubic, MoSi$_2$-/Ti$_2$Ni-type</td>
</tr>
</tbody>
</table>

Hydrogen pressure does not increase significantly when charging a metal hydride with hydrogen gas. This is because of the phase transition taking place during hydrogen absorption, as discussed in the thermodynamic measurement section. Several families of intermetallic compounds listed in Table 2.5 are interesting for hydrogen storage application. Most metallic hydrides absorb hydrogen up to a hydrogen-to-metal ratio of H/M = 2. Greater ratios up to H/M = 4.5, for example BaReH$_9$ [68].

Among the most studied hydrides are MgH$_2$ and PdH$_{0.7}$, with hydrogen gravimetric density of 7.6 wt% and 0.6 wt%, and dehydrogenation temperature of 330°C and 25°C at 1 atm, respectively [50,60]. The theoretical enthalpy of the transfer of hydrogen into the Mg metal lattice is -74.5 mol$^{-1}$ [60].
Fig. 2.11 (a) and (b) shows the crystal structures of palladium and palladium hydride, while Fig. 2.11 (c) and (d) shows the crystal structures of magnesium and magnesium hydride. These crystal structures were created using the Materials Studio® software [69]. As palladium hydride is an interstitial hydride, the crystal structure remains cubic even after the metal has soaked up hydrogen, with the hydrogen residing in the interstitial sites. The magnesium, on the other hand does undergo a phase transition when it is hydrogenated. The crystal structure of metallic magnesium is hexagonal, but the hydride of magnesium assumes the TiO$_2$ rutile-like crystal structure (tetragonal).

Quantum chemical calculations have been used to follow the expansion of the crystal lattice of MgH$_2$ as hydrogen was absorbed into its bulk crystal structure, and results suggested that kinetic constraints at near-ambient pressure mean that the time taken for absorption and desorption is in the range of hours, which makes pure MgH$_2$ unsuitable
for mobile applications [50,60]. Many investigations on MgH$_2$ have focused on improving the kinetics of hydrogen absorption and desorption, and reducing the operating temperature. These have been accomplished to some extent by modifying the surface, reducing grain size, and introducing catalysts.

During the early stages of hydrogen storage research, palladium has received some attention for its potential as an onboard hydrogen storage material. However, the fact that it only stores 0.6 wt% of hydrogen combined with the high cost of the metal makes it a rather unrealistic option in large-scale production for mobile applications [60].

2.10.3 Complex hydrides

Complex hydrides are hydrides thought to be involved in some kind of complex bonding. The complex hydrides typically involve light atoms, which, in general, would seem suitable for high hydrogen-to-metal ratios. Hydrogen is often not located in the most obvious interstitial sites, but rather near certain lattice atoms as a result of favored bonding to the atoms in these locations [60]. Examples of complex hydrides are LiBH$_4$ [70], NaAlH$_4$ [71], and LiAlH$_4$ [72]. The theoretical gravimetric density of LiBH$_4$ is 18 wt%. However, complex hydrides are often non-reversible, and the complex sequences involved in dehydrogenation often makes the hydrogen release a slow process, despite the presence of catalysts such as Ti [73]. They are, therefore, currently seen as unlikely candidates for mobile applications, where there is often a need for hydrogen on demand, especially during the acceleration phase [60].

In the case of lithium borohydride, the dehydrogenation which occurs at 300°C in the presence of SiO$_2$ catalyst releases 13.8 wt% of hydrogen as follows [60]:
Chapter 2

2LiBH$_4$ $\rightarrow$ 2LiH + 2B + 3H$_2$

It has been found that it is possible to reverse the process in order to rehydrogenate the system, but complete reversibility has so far only been achieved at a pressure of 100 atm and a temperature of 550°C [60].

In summary, literature reviews of research and development on metal-hydrides suggest that hydrides are, in general, very effective for storing large amounts of hydrogen (high volumetric densities) in a safe and compact way. However, all the currently known reversible hydrides found to be working around ambient temperature and atmospheric pressure consist of transition metals and, as a consequence, the gravimetric hydrogen density is limited to less than 3 wt%.

2.11 Optical properties of metal hydride thin films

2.11.1 Developments of hydride-based switchable mirrors

In 1995 during a search for high temperature superconductors, a research group in Amsterdam discovered a significant change in the optical properties of metal hydride films of yttrium (Y) and lanthanum (La) around their metal-insulator transition [74]. They found that the dihydrides are metallic in appearance, while the trihydrides are semiconductors and transparent in the visible range. Furthermore, the transition from the metallic to the transparent state is reversible by changing the surrounding hydrogen gas pressure at room temperature. In the transparent state, YH$_3$ is yellowish in color, while LaH$_3$ is reddish. It was later found that all the trivalent rare-earth hydrides and even some of their alloys exhibit switchable optical and electrical properties [75,76]. A surprising fact is that these films retained their structural integrity, even though they
expanded by about 15% during hydrogenation from the metallic to the hydride state. The ability to tailor their properties by alloying and the ease of continuously changing their hydrogen content by varying the hydrogen pressure made them an invaluable tool for fundamental research [50]. They also offer the possibility of investigating the continuous metal-insulator quantum phase transitions. In this thesis, however, the scope of this review will be focused on the optical properties of these films, as the applications emphasis for thin film hydrides in this thesis is focused on hydrogen storage and switchable mirrors.
2.11.2 The classical rare-earth (RE) switchable mirrors

Film deposition and electrical characterization of RE and RE hydrides were first reported in the 1970s [77], but the hydrides were not phase-pure, due to the limited quality of the vacuum systems at those times, since the base pressure required to fabricate pure RE film has to be below $10^{-5}$ Pa [78]. Various physical vapor deposition methods, such as molecular beam epitaxy [79], sputtering [76] and pulsed laser deposition [80], had been used to fabricate the films, and they did not seem to influence the characteristics of the films much. RE films are very reactive to oxygen in the air, and therefore, capping layers such as palladium [78] and gold [79] are commonly used to prevent oxidation and at the same time function as catalysts for hydrogen dissociation and absorption [81]. The capping layers have to be deposited at room temperature to prevent the formation of a RE-Pd alloy which could block hydrogen diffusion [82]. Among the material systems that have been investigated for switchable RE hydrides were the Pr, Sm, Gd, and Dy hydrides [50], although the most common material system was the Y hydrides, and so we will use them to represent the RE hydrides for convenience.

2.11.2.1 Optical properties of RE-switchable mirrors

The Y film changes smoothly and reversibly from the metallic state to the transparent state between the dihydride ($\text{YH}_2$) and the trihydride ($\text{YH}_3$) phase. The optical transition is always accompanied by an electrical transition from metallic to semiconducting when going from the dihydride to the trihydride phase [83].
2.11.2.2 Theoretical modeling for the RE-switchable mirrors

The transparency of the YH$_3$ film first discovered in 1995 [74] was puzzling because band structure calculations [84,85] suggested that YH$_3$ had a large band overlap of 1.5 eV. The strong electron-correlation model [86,87] which was originally developed for high-temperature superconductors hinted that there might be significant charge transfer from yttrium to the hydrogen and that hydrogen did not enter the film as protons but rather as a negatively charged ion with an effective charge of about -0.5e [88]. Furthermore, results from angular resolved photoemission spectroscopy suggested the existence of a strongly correlated electron system [89]. More recently, calculations based on the GW approximation (GWA) yielded an insulating ground state for YH$_3$, and the calculated dielectric function agreed reasonably well with the experimental data for YH$_3$ and LaH$_3$ [90,91].
2.11.3 Magnesium-based thin films

Despite the RE thin films exhibit optical switching, the transparent state is color-tinted. It would be of advantage, particularly from a technological viewpoint to have hydride film that can switch from a metallic state to a transparent state that is color neutral. A group of researchers at Philips Research in 1997 discovered that magnesium films have such desirable switchable optical property [76], and the magnesium films are regarded as second generation switchable mirrors. As mentioned in an earlier section of this chapter, Mg is considered to be one of the most important candidates for reversible storage of hydrogen due to its light weight, low cost, and relatively high gravimetric hydrogen capacity of 7.6 wt%. Given its importance, the optical properties of MgH$_2$ thin films have been studied in detail [92], and it was found that MgH$_2$ is a highly transparent insulator with an optical band gap of 5.6 eV (221.65 nm), which is in good agreement with GW band structure calculations. Magnesium-based alloys such as magnesium nickel (MgNi$_2$) were also found to have switchable mirror properties with an estimated band gap of 1.6 eV [93].

2.11.4 Potential applications of switchable mirrors

2.11.4.1 Switchable mirrors as indicator layers

The fact that switchable mirror films have optical properties that depend strongly on hydrogen concentration means that they can be used as two-dimensional hydrogen concentration indicators. The simplest application is to monitor hydrogen diffusion in switchable mirror themselves [50]. Fig. 2.12 shows a top-view image of an actual setup used in one of the experiments during the course of this PhD degree to study the evolution of the hydrogen concentration in a hydride film as a function of time as the
temperature was raised above the desorption temperature of the hydride film. The change in the intensity of the transmitted light through the semitransparent hydride film was continuously monitored by a two-dimensional imager. The interior of the custom-built hermetic hydrogen optical cell consisted primarily of a thermocouple, which was used to monitor and control the cell temperature, and a pair of sample arresting bars.

Fig. 2.12 Setup in which a hydride switchable mirror was used to monitor hydrogen diffusion. The image was a snapshot taken from a real-time video stream recorded by the imager.

2.11.4.1 Combinatorial research – hydrogenography

In combinatorial research, a large number of compounds with different compositions are synthesized and characterized in parallel. Combinatorial research has been used in such areas as biochemical and pharmaceutical research with great success and efficiency, and it has recently been applied to material science and engineering, given the ever greater importance of structure-property relations and the increasing complexity of the material systems involved [94–96].

A way to produce many thin film compositions simultaneously is to use the compositional gradients that develop across a wafer in a co-deposition process in the absence of substrate rotation [97]. Gremaud et al. has recently demonstrated that a
combinatorial technique known as hydrogenography could be used to optically measure the enthalpies (and entropies) of hydrogenation of thousands of alloy compositions simultaneously [97]. Quaternary metal hydride Mg-Ni-Ti-H was used to illustrate the principle of hydrogenography. Mg-Ni-Ti gradient films were sputtered on a 3-inch sapphire substrate by means of tilted Mg, Ni, and Ti magnetron sputter sources positioned every 120° in a circle around the substrate [97], and the film was capped with 20 nm Pd to promote hydrogen dissociation and to prevent oxidation of the underlying film. The sample was transferred into an optical cell to allow monitoring of optical transmission during hydrogenation. The transmitted light intensity was continuously monitored by a charge coupled display (CCD) camera as hydrogen pressure of the optical cell was gradually increased. An example of a typical image captured by the CCD camera at a hydrogen pressure of $3 \times 10^3$ Pa and a temperature of 60 °C is shown in Fig. 2.13. By continuously recording the optical transmission as a function of increasing hydrogen pressure, a pressure-composition isotherm map can be constructed based on the Lambert-Beer law [97]. With such a map, Gremaud et al. [97] were able to identify a composition range of alloys that form hydrides with enthalpies significantly less negative than those of either MgH$_2$ or Mg$_2$NiH$_4$.

Fig. 2.13 Hydrogenography: intensity image of the hydrogen-induced optical transmission during hydrogenation [97].
2.11.4.2 Fiber optic hydrogen sensor

For society to accept the hydrogen-based economy there is a need for sensitive, fast, reliable, and cheap hydrogen sensors. The current commercial hydrogen detectors are rather bulky and expensive, and therefore, are not suitable for widespread use, especially in the transportation sector [98,99]. Also, most of the commercial hydrogen detectors currently available are based on electrical measurement which might not be desirable in potentially explosive environments [98].

These disadvantages can be solved by using an optical detection system [100–104]. The optical detection systems investigated were mainly based on optical fiber where the end of an optical fiber is coated with a hydrogen-sensitive layer, and the changes induced in the optical properties of the active layer during adsorption of hydrogen are detected optically at the other end of the fiber. Optical fiber sensors, therefore, have the advantage of being simple yet very sensitive, cheap, immune to electromagnetic noise, explosion safe, and allow for multiple parallel sensing with one central detector [50].

The optical fiber sensor head considered here is shown in Fig. 2.14. The top layer is a protective coating and it serves to prevent degradation of the film by condensed water. The effect of the coating on the loading and unloading behavior of the film is found to be negligible [98]. Beneath the optional coating is a palladium layer, which catalyzes the hydrogen absorption by the switchable mirror and prevents the oxidation of the active optical layer. The ideal thickness of the palladium layer in this application is around 50 nm, which makes the palladium layer optically dense. A larger layer thickness can cause microcracks during the expansion of the film upon hydrogen loading [98]. The thickness of the palladium layer may be reduced in the case where the switchable mirror beneath the palladium is not completely transparent in the hydrogenated state.
2.12 Sample preparation methods

We now turn our attention to the sample preparation methods. Among the methods commonly used to prepare the samples for hydrogen storage are the wet chemical method, ball milling, and various deposition techniques such as pulsed laser deposition or electron-beam evaporation for thin film samples. Ball-milling techniques and physical vapor depositions techniques will be reviewed in greater detail, as they are the primary sample preparation methods used in this thesis. Greater emphasis is placed on the thin film deposition of samples in Chapter 5 and 6, which were prepared by physical vapor deposition techniques (pulsed laser deposition and thermal evaporation, respectively). Thin film growth will also be reviewed later in the chapter.

2.12.1 Nanopowder synthesis via ball milling

The ball-milling method is a top-down approach toward manufacturing nanomaterials. The primary objectives of milling have been size reduction, mixing, and change in particle morphology. It was only in recent decades that mechanical milling has been used in the attempt to synthesize new alloys, compounds, and nanomaterials. Ball-
milling equipment can be classified according to the way in which mechanical forces are applied: (1) between two solid surfaces (crushing, shearing), and (2) at one solid surface (impact). The milling in ball mills combines both crushing/shearing and impact forces combined in various proportions, depending on the equipment used. The ball-milling technique can be regarded as a form of kinetic processing because there is a transfer of kinetic energy from the balls (grinding media) into the powdery sample. There are many different designs of ball mills, which can be used for processing of advanced materials. Among them are [20]:

- Tumbler ball mills
- Szegvari attritor vertical mills
- Planetary ball mills
- SPEX model mills
- A.O.C. magnet-controlled mechanical model mill (Uni-Ball magnetomill)
- A.O.C. electric discharge-assisted mechanical mill
- ZOZ continuous-fed horizontal mill

The tumbler and planetary ball mills will be reviewed in greater details as they are the types used in this thesis.

### 2.12.1.1 Tumbler ball mill

In the tumbler ball mill, the grinding balls impact upon the powder sample when the milling jar rotates about a horizontal axis. The most likely trajectory of a ball inside the rotating milling jar is such that it falls freely under gravity, impacting the powder sample and other balls underneath it. The balls may also roll down the inner wall of the jar and produce shear forces on the powder sample trapped between the inner wall and
the ball. The kinetic energy, $E_{\text{kin}}$, transferred when a ball of mass $m$ impacts on the powder sample is [105]

$$E_{\text{kin}} = \frac{1}{2} m (gr)^2$$  \hspace{1cm} (2.12)

where

$t$ is the time-of-flight of the ball during free fall

$g$ is the Earth’s gravitational acceleration (9.81 m s$^{-2}$)

Given the limited diameter of the milling jar used in the laboratory (which in turn limits the time-of-flight), a tumbler ball mill in a laboratory setting is therefore often regarded as a low-energy mill.

### 2.12.1.2 Planetary ball mill

In planetary ball mill, the force acting on the balls is increased. A centrifugal force of 50 times the gravitational force can be easily achieved. The motion of the shell and the balls in a planetary mill is shown in the schematic diagram in Fig. 2.15. The size of a planetary ball mill will be smaller than the size of a drum (tumbler) ball mill of the same energy. Planetary ball mills can be considered as medium to high energy ball mills, however, milling times needed to process submicron size and nanostructured powders may be long.
2.12.2 Thin film fabrication via physical vapor deposition

In the previous section, we have reviewed ball milling, which is a “top-down” approach to synthesis nanomaterials. We now turn our attention to thin-film deposition, which is a “bottom-up” approach, i.e., one that relies much on the properties of atoms and molecules that allow them to interact both among themselves and with the substrate into some useful structures based on the property of self-organization or self-assembly. This approach can be used to create nanodimensional materials (in thickness, in the case of thin film) to yield quantum effects unseen in their bulk counterparts, which can be important for the improvement of hydride materials. Thin film deposition also allows the microstructure, surface morphology, and electrical and optical properties to be varied to a certain extent by the deposition conditions and the substrate preparation methods [106].

Deposition processes can be generally divided into two types:

1. those involving droplet transfer (e.g., plasma spraying, and arc spraying);

2. those involving atom-by-atom transfer (e.g. physical vapor deposition, chemical vapor deposition, and electrodeposition).
The main disadvantage of the droplet transfer process is the tendency to create porosity in the final deposit, which affects the final properties of the films. There are also significant differences as well among the atom-by-atom transfer processes. The physical vapor deposition (PVD) process offers greater flexibility in controlling the structure, properties, and deposition rate relative to the chemical vapor deposition and the electrodeposition techniques [106].

PVD is a general term used to describe the deposition of thin solid films by the condensation of a vaporized form of a solid material onto various surfaces. It involves physical ejection of material as atoms or molecules, and condensation and nucleation of these atoms onto a substrate. The PVD can be further divided into three different processes [106]:

Evaporation – In the evaporation process, heating methods such as resistive heating, radiation, electron beam, laser beam, and arc discharge are used to heat the source material to produce deposition vapors. The deposition process is usually carried out under vacuum conditions (typically $10^{-5}$ to $10^{-6}$ Torr), so that the evaporated atoms undergo an almost collision-free line-of-sight transport from the source to the substrate.

Sputtering – In the sputtering process, positive gas ions (usually argon ions) produced in a glow discharge (gas pressure 20 to 150 mTorr) bombard the source material known as the target, dislodging groups of atoms which then pass into the vapor phase and are deposited onto the substrate. Sputtering is an inefficient way to induce a solid to vapor transition, and therefore phase change costs range from three to ten times larger than for evaporation [107].
Ion plating – In the ion plating process, the source material is vaporized in a similar way as in the evaporation process, except it passes through a gaseous glow discharge on its way to the substrate, which causes ionization of some of the vaporized atoms. Ion plating can thus be regarded as a hybrid of the evaporation and sputtering processes.

Pulsed laser deposition (PLD) which is an evaporation technique will be reviewed in greater detail in the following section as it a process used to fabricate thin films in this PhD study (in addition to thermal evaporation).

2.12.2.1 Pulsed laser deposition

The pulsed laser deposition (PLD) technique was first used by Smith and Turner [108]. In PLD, high-power laser pulses ablate a small amount of material from a solid target when a focused laser beam is absorbed by a small area of the target surface. During the ablation, chemical bonds within the solid target are broken, and the material is evaporated in a certain direction. The resultant evaporated material is comprised of ions, molecules, neutral atoms, and free radicals of the target material in their ground and excited states. This further absorbs a large amount of energy from the laser beam producing an expansion of hot plasma (plume). The plume then expands away from the target with a velocity distribution of different particles in the forward direction [109]. The ablated species finally condense on a substrate, placed at an angle opposite to the target, and eventually form a thin film.

The ablation process takes place inside the vacuum chamber, either under base vacuum or in the presence of a gas. A laser beam is focused on the surface of a target through a transparent fused silica window in the chamber. The stoichiometry of the material is
preserved in the ablation process, owing to the simultaneous evaporation of all the components in the target, irrespective of their binding energies. This is mainly due to the fast and intense heating of the target surface by the laser beam. The accumulation of target material on the substrate from a large number of laser pulses leads to the gradual formation of a film.

Deposition by laser ablation is widely known to produce quality films of various kinds, including semiconductors, high T\textsubscript{c} superconductors, ceramics, and ferroelectrics [110–113]. Recently, PLD has also been used to synthesize nanotubes [114], nanopowders [115], and quantum dots [116].

The parameters that can be controlled during PLD are the fluence (energy per unit area), wavelength, pulse duration, pulse repetition, and preparation conditions, as well as system configurations, such as target to substrate distance, substrate temperature, and pressure [117].

A typical setup configuration for laser ablation and thin film deposition is shown schematically in Fig. 2.16. Fig. 2.17(a) shows the actual PLD setup in our laboratory along with the illustrated laser path. The pulsed laser is a lambda Physik LPX 305 excimer laser with a wavelength of 248 nm and a maximum energy of 1.2 J per pulse. A close-up view inside the vacuum chamber shows the target holder and the substrate holder [Fig. 2.17(b)]. The target material usually rotates during pulsed laser ablation while the substrate holder can set to rotate during film deposition, if necessary. The target-to-substrate distance is adjustable, depending on the required film deposition conditions.
Fig. 2.16 Schematic diagram showing the essential components of a typical pulsed laser deposition system.

Fig. 2.17 (a) The PLD setup in our laboratory, and (b) view inside the vacuum chamber showing the substrate holder and the target holder.
Although laser deposition is an attractive approach for the synthesis of high-purity metal alloys and compound films, it suffers from the following limitations [106]:

- Small size of the laser impact spot which results in small deposition film area, restricting the number of samples that can be fabricated in a single run with good uniformity in film thickness.

- It is not always possible to find a laser with a wavelength compatible with the absorption characteristics of the material to be evaporated because material properties, such as reflectivity and the absorption coefficient of a solid target, depend on the wavelength of the laser used. Thus, the wavelength of the laser has a significant effect on the yield of the ablated particles.

- The ‘splashing effect’, which involves the production of microparticles between 0.1 and 10 µm in size, and thus diminishes film quality [118].

- Complex transmission and focusing systems need to be employed to direct the beam from the laser located outside the vacuum system onto the evaporant placed inside the system. This involves special optical path designs and increases the cost of the setup. Also, a window material which efficiently transmits the wavelength band of the laser must be found and mounted in such a way that it is not rapidly covered up by the evaporated material.

- Energy conversion efficiency is very low – usually around 1 to 2%. 
The main advantages of this technique are:

- Excellent transfer of stoichiometry between the target and the film;
- The production of high-energy species, which enhances film quality.

2.12.2 Thin film growth and microstructural evolution

The early stages of growth of a solid film on a given substrate surface begin with nucleation, and so the study of nucleation and the early stages of growth is essential to our understanding of the science and technology of thin films. The primary deposition parameters that have been found to affect the growth of films are the source material, the growth temperature, the substrate material, and surface cleanliness, crystallinity, and orientation [106].

There are essentially three modes by which the film material can grow on the substrate surface during deposition. They are the three-dimensional (3D) growth mode, two-dimensional (2D) growth mode, and the Stranski-Krastanow (S-K) ‘quantum dot’ growth mode which is a combination of the first two modes [106].

Nucleation of the source material on a substrate surface corresponds to a phase transition in which the vapor or liquid phase atoms are deposited at a coverage yielding sufficiently high 2D spreading pressures that the local density fluctuations in the 2D gas give rise to the formation of stable clusters or nuclei. ‘Stable’ in this sense refers to clusters which have a higher probability of growth than of dissociation.

The three types of well known growth mode evolution are illustrated schematically in Fig.2.18. During the 3D growth, also known as the Volmer-Weber growth mode or island growth, stable clusters develop into 3D islands, which, in turn, coalesce to form a
continuous film. 3D growth often occur when the adatoms are much more strongly bound to each other than to the substrate surface, as in the case of metallic films on insulating substrates (such as silicon dioxide), or when the substrate surfaces are contaminated. In the 2D layer-by-layer (atomic layer by atomic layer) growth mode (Frank - van der Merwe), the adatom-adatom binding energies are equal to or less than those between the adatoms and the substrate. Common example of 2D growth mode are metal-on-metal deposition (such as gold on silver), metal-on-semiconductor deposition (such as iron on GaAs), and semiconductor-on-semiconductor deposition (such as silicon on silicon). The S-K growth mode was predicted by Stranski and Krastanow in 1938 [119]. An example of the S-K growth mode is germanium grown on a silicon <001> surface. In this growth mode, the initial growth is dominated by the 2D layer-by-layer growth mode, but makes a transition to 3D island growth mode when the growth becomes energetically unfavorable. This occurs when the coverage film thickness reaches one or two atomic monolayers (ML). In other words, the growth transition is driven by a decrease in the total system energy [120,121]. An atomic monolayer is a single closely packed layer of atoms [122]. The elastic strain energy, $E_{\text{elas}}$, has been found to be proportional to the product of the square of the lattice parameter mismatch between the film and the substrate, $\varepsilon$, and the thickness of the film, $x$ [123]. That is,

$$E_{\text{elas}} \propto \varepsilon^2 x$$  \hspace{1cm} (2.13)

The lattice parameter mismatch, $\varepsilon$, is defined as

$$\varepsilon = (a_f - a_s) / a_s$$  \hspace{1cm} (2.14)

where $a_f$ and $a_s$ is the lattice parameter of the film and substrate, respectively.
Fig. 2.18 Graphical representations of the three solid-film growth modes and their evolution as a function of the film thickness, $x$, in the unit of monolayers (adapted from Ref. 106).

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CHAPTER 3

Magnesium hydride catalyzed by Ti and Ni/Ti

From the literature review covered in Chapter 2, magnesium hydride (MgH$_2$) is among the potential hydrides for mobile application, albeit it has a high temperature of hydrogen desorption of around 300 °C at ambient pressure. In this chapter, the desorption capacity, thermodynamics, and kinetics of Ti- and Ni/Ti-catalyzed Mg hydrides were investigated using Sieverts-type apparatus and differential scanning calorimetry. The addition of Ti and Ni as catalysts has been found to moderately improve the thermodynamics (lowered desorption temperature) while significantly increasing the kinetics. A combination of Ti and Ni is a more effective catalyst than either Ti or Ni alone, suggesting the existence of a synergetic effect. The parameters associated with the hydrogen desorption of MgH$_2$ characterized in this chapter are the hydrogen capacity ($H_{cap}$), the desorption time ($t_{release}$), the enthalpy ($\Delta H$), the entropy ($\Delta S$), and the activation energy ($E_A$).
Chapter 3

3.1 Introduction

Development of a hydrogen storage system suitable for light-duty automotive vehicles is essential to the realization of a hydrogen economy. As discussed in Chapter 2, the MgH$_2$ system is one of the promising metal hydrides that can be used as a hydrogen storage medium because it can store hydrogen reversibly up to 7.6 wt% and has a high volumetric hydrogen density of 106 kg H$_2$ m$^{-3}$. Furthermore, magnesium is abundant and inexpensive.

However, the use of pure magnesium as a practical hydrogen storage material is hindered by its slow sorption kinetics and high temperature of hydrogen release. It has been previously demonstrated that transition metal additives can significantly improve the kinetics of MgH$_2$ [1–4]. Also, it is interesting to note that effective catalysis does not require covering the entire metal surface by an overlayer of a catalyst [5,6]. Instead, particles of the catalyst tens of nanometers in size are sufficient, when uniformly distributed on the metal surface [1]. This process can be explained by a “spill-over” phenomenon, in which a catalyst on the surface of a host metal dissociates hydrogen molecules into hydrogen atoms which then diffuse into regions of the metal where dissociative adsorption does not easily occur, such as those covered by oxides [7]. In other words, there is no need for the surface of the magnesium to be very active and free of oxides because it is the catalyst that dissociates or recombinates the hydrogen molecules. Pelletier et al. has studied the hydrogen desorption mechanism in MgH$_2$-Nb nanocomposites, and it was found that the hydrogen desorption involved the formation of a short-lived metastable niobium-hydride phase which acts as a gateway through which the flow of hydrogen out of the MgH$_2$ occurs [8]. Larsson et al. carried out first-principles calculations based on density functional theory on MgH$_2$ nanoclusters with
the aim of gaining a better understanding of the role of catalysts in dehydrogenation, and the simulation results seemed to support the gateway hypothesis of dehydrogenation mentioned above, where transition metals, in general, would act as catalytic centers for hydrogen atoms by continuously attracting new hydrogen atoms from the rest of the cluster as the hydrogen desorbs [9].

Titanium (Ti) and nickel (Ni) have been found to be very effective catalysts for the MgH$_2$ system [2,10]. Ref. 11 reported that for the Ti-incorporated Mg(001) surface, the activation barrier decreases to 0.103 eV due to the strong interaction between the molecular orbital of hydrogen and the d-metal state of Ti, which could explain the experimentally observed improvement in absorption kinetics of hydrogen when Ti have been introduced into magnesium.

In the ball-milled Ti-catalyzed MgH$_2$ system, however, the addition of Ti did not change the thermodynamic properties of MgH$_2$, even though there was a significant reduction in the activation energy of hydrogen desorption [2]. Further improvement of the hydrogen storage properties could be achieved by adding in another effective catalyst, such as Ni, which is reported to play a vital catalytic role in promoting the hydrogenation kinetics of Mg-based alloys [2,12]. An electrochemical study of Mg-Ni-Ti ternary alloys as hydrogen storage electrodes have been reported [13]. However, there have only been a few studies on the synergetic catalytic effects of the elements Ni and Ti on Mg hydride, and so far, within such studies, there has been no quantitative analysis based on either the van’t Hoff equation or the Kissinger equation.

In this work, the hydrogen desorption performance of nanocrystalline Mg hydrides catalyzed by elemental Ti as well as by the combination of elemental Ni and Ti have been studied using Sieverts-type apparatus and differential scanning calorimetry (DSC).
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The hydrides were characterized in terms of the hydrogen storage capacity, desorption time, thermodynamics and kinetics, and activation energy. In this work we focused on the desorption behavior of MgH$_2$ because it is more important than the absorption behavior as far as mobile applications are concerned, a view shared by Czujko et al. [14].

### 3.2 Experimental

The elemental powders used for the experiments were purchased from Sigma–Aldrich. The average particle size of the as purchased Ti, and Ni was about 7 µm, and 3 µm, respectively. The following ratios were used for the catalyzed Mg hydrides: MgH$_2$-$x$ at.% Ti ($x = 1$ and 5) and MgH$_2$-Ni/Ti (Ni:Ti = 1:1 in molar ratio, with 16.7 at.% Ni, and Ni:Ti = 4:1, with 26.7 at.% Ni). The samples were prepared by ball milling under hydrogen atmosphere at an initial pressure of about 7 atm for 35 hours. The ball-milling equipment was a magnetically controlled Uni-Ball-Mill with a rotational speed of 60 rpm. All powders were handled in a glove box with an argon atmosphere to prevent the oxidation of the samples.

The phases present in the ball-milled samples were investigated by X-ray diffractometry, using a GBC diffractometer with Bragg-Brentano optics, Cu Kα radiation ($\lambda = 0.15405$ nm) and graphite monochromator. Scans were performed at a rate of 2° min$^{-1}$ and 0.02° step size. Search-and-matches were performed using the Traces™ software and the 2007 ICDD (International Center for Diffraction Data) search-match database.
Transmission electron microscopy (TEM) was performed using a 200 keV JEOL 2011 analytical instrument. TEM samples were prepared by dispersion of dry powders onto holey carbon support films on 200 mesh Cu grids. In order to investigate the morphology and crystallography of the products, bright-field imaging was combined with selected area electron diffraction (SAED) and with dark-field imaging.

The dehydrogenation characterizations were performed using a Sieverts-type apparatus (volumetric method). The Sieverts-type apparatus was used to measure the hydrogen capacity \( H_{\text{cap}} \), the desorption time \( t_{\text{release}} \), the enthalpy \( \Delta H \), and the entropy \( \Delta S \).

The Sieverts-type apparatus used in this work was manufactured by the Advanced Materials Corporation (USA). The unit is known as the “Ultra-High Pressure Gas Reaction Controller” and the system includes a reaction sample chamber for housing the test sample and a furnace. The system has been designed to be computer-controlled using the software known as “GrcLV”, which was developed under National Instruments’ LabVIEW. The gas reaction controller unit was connected to the reaction sample chamber which housed the hydride test sample. The temperature of the sample chamber was controlled by a 300 W furnace, which was linked to the GrcLV software.

The as-milled samples were activated at 380 °C under a hydrogen pressure of 30 atm and evacuated at the end of 1 hour. The hydrogen capacity was calculated by the mass of MgH\(_2\) plus the catalysts. The activation energy \( E_A \) for the hydrogen desorption kinetics was obtained using DSC techniques (TA Instruments Q100) with different linear heating rates under an argon flow rate of 50 mL min\(^{-1}\). The argon pressure inside the DSC cell was 1.0 atm.
3.3 Results and discussion

3.3.1 Phase structures

Mechanical milling of magnesium hydride with the 3d-transition metals leads to various products, depending on the relative affinity of the 3d-metal to hydrogen. Fig. 3.1 shows the XRD spectra for the 35-hour ball-milled MgH$_2$ along with the other four MgH$_2$ samples with various percentages of Ti and Ni additives. The XRD spectra were matched against the ICDD database. The crystal structure present in the as-milled MgH$_2$ sample is primarily tetragonal MgH$_2$ (12-697) with some amount of orthorhombic MgH$_2$ (51-621). A small amount of magnesium oxide (MgO) was also detected in the sample, and the source of oxygen is likely to be from the surfaces of the ball-milling jar as well as the grinding balls. Powder refinement based on the Pawley algorithm was used to refine the lattice parameters and estimate the mean crystallite size of the tetragonal MgH$_2$ phase in the ball-milled sample using the Reflex module within Materials Studio (Accelrys Software Inc) [15]. The symmetry of the tetragonal crystal structure imposes constraints on the lattice parameters such that $a = b$.

Fig. 3.2 shows a comparison between the experimental data and the simulated spectrum from the powder refinement results, indicating that there was a good match between the simulated spectrum and the experimental data, including the relative peak intensities. Peaks not belonging to tetragonal MgH$_2$, such as the one from MgO ($2\theta = 43^\circ$), were excluded from the refinement to maximize the accuracy in the determination of the lattice parameters and crystallite size of the tetragonal MgH$_2$, which was the primary phase in the sample. Fractional coordinates were kept fixed during the optimization of the lattice parameters. The inset in Fig. 3.2 shows the tetragonal crystal structure of MgH$_2$ with the lattice parameters $a$, $b$, and $c$ indicated. These lattice parameters were
determined based on the optimum agreement between the simulated powder diffraction spectrum and the experimental data:

\[ a = b = 4.5110 \text{ Å} \quad c = 2.9984 \text{ Å} \]

The lattice parameters of tetragonal MgH\(_2\) (12-697) in the ICDD database are

\[ a = b = 4.517 \text{ Å} \quad c = 3.0205 \text{ Å} \]

The mean crystallite size of the ball-milled MgH\(_2\) (which is associated with the broadening of the XRD peaks) was estimated to be:

\[ L_a = L_b = 59.9279 \text{ Å} \quad L_c = 58.3366 \text{ Å} \]

The XRD spectrum for the MgH\(_2\) + 1 at.\% Ti did reveal a small but detectable titanium hydride (TiH\(_2\)) peak around \(2\theta = 34.94^\circ\), and the peak intensity increased significantly in the 5 at.\% Ti sample. The existence of TiH\(_2\) along with the 20 peak positions at 34.9° and 58.7° were consistent with XRD results reported by Liang et al [2]. In the Ni/Ti samples, the existence of Ni, TiH\(_2\) was detected, as well as a relatively small fraction of magnesium nickel hydride (Mg\(_2\)NiH\(_4\)). The presence of Mg\(_2\)NiH\(_4\) has also been reported for an MgH\(_2\) sample ball milled with Ni [2]. Also, it should be noted that there was a preferred orientation in the tetragonal crystal structure of the MgH\(_2\) along \(2\theta = 35.97^\circ\) for both the Ni/Ti samples. Such a shift in preferred orientation was not observed for the Ti samples, or at least not obvious.
Fig. 3.1 X-ray diffraction patterns for the pure MgH$_2$ and the MgH$_2$ with Ti and Ni additives after 35 hours of ball milling. The samples with the additives Ni:Ti = 1:1 and Ni:Ti = 4:1 have Ni contents of 16.7 at.% and 26.7 at.%, respectively.

Fig. 3.2 Powder refinement optimization result for the as-milled MgH$_2$ sample. The inset shows the MgH$_2$ tetragonal crystal structure along with the labeling of the lattice parameters $a$, $b$, and $c$ (with the symmetry constraint $a = b$).
3.3.2 TEM analysis

TEM bright and dark-field analysis confirmed that the mean crystallite size of the ball-milled tetragonal magnesium hydride was within the range of 5 to 15 nm, with most crystallites being less than 10 nm in size. This observation is in agreement with the mean crystallite size estimation provided by the Pawley refinement, which was about 6 nm (60 Å). A bright-field TEM image of the MgH$_2$-Ni/Ti (Ni/Ti = 4/1) sample after ball-milling is shown in Fig. 3.3(a). Fig 3.3(b) shows the dark-field image obtained using MgH$_2$ (110) and (101) reflections, according to the circled region in the inset selected area electron diffraction (SAED) pattern. The predominantly fine structure of the electron diffraction rings is consistent with the presence of very fine, randomly oriented MgH$_2$ crystals.
3.3.3 Hydrogen desorption characterizations

3.3.3.1 Hydrogen desorption capacity

Fig. 3.4 shows the hydrogen desorption capacity that results from ramping up the temperature to 400 °C under 0.1 atm hydrogen pressure. The measured hydrogen desorption capacity, $H_{\text{cap}}$, was 4.9 wt%, 4.5 wt%, and 2.9 wt% for the 1 at.% Ti, the 5 at.% Ti, and the Ni–Ti samples, respectively, as is tabulated in Table 3.1. Fig. 3.4 also gives us a qualitative indication that the addition of Ti leads to a significantly decrease in the desorption temperature of MgH$_2$, and samples with Ni–Ti additives seem to have the lowest $T_{\text{des}}$. It cannot be too strongly emphasized, however, that the exact $T_{\text{des}}$ of the
samples has to be determined via the PCI curves under equilibrium hydrogen pressure and constant temperature.

### 3.3.3.2 Thermodynamic measurements

The thermodynamic properties of the samples, including the pure MgH$_2$, were obtained from the PCI curves at various fixed temperatures and are tabulated in Table 3.1. The pressure–composition isotherm (PCI) desorption curves for the MgH$_2$–Ni/Ti (Ni/Ti = 4/1) sample at temperatures of 340 °C, 360 °C, 400 °C, and 420 °C are shown in Fig. 3.5. Note that the PCI curves should have positive gradients in the β-phase region instead of negative gradients. The reason for the negative gradient tendency was because there was some inaccuracy in the automated compensation algorithm for the hydrogen capacity values ($H_{\text{cap}}$) as the equilibrium pressure changes. Nevertheless, the inaccuracy in the compensation algorithm did not affect the reliability of the absolute plateau pressure measurements which were used to calculate the thermodynamic properties such as the $T_{\text{des}}$, as the pressure readings were taken directly from a well calibrated pressure-transducer linked to the sample chamber in which the sample resides.

The dissociation enthalpy ($\Delta H$) and the entropy ($\Delta S$) were obtained from the van’t Hoff equation, as discussed in Chapter 2:

$$\ln\left(\frac{P_{\text{eq}}}{P_{\text{r}}}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$  \hspace{1cm} (3.1)

where $P_{\text{eq}}$ is the equilibrium pressure, $P_{\text{r}}$ is the reference pressure (taken to be 1.0 atm herein), $T$ is the isothermal temperature, and $R$ is the gas constant.
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Fig. 3.4 Hydrogen desorption capacity measured using the volumetric method by ramping the sample temperature from room temperature to 400 °C at 0.1 atm hydrogen pressure.

Fig. 3.5 The pressure-composition isotherm (PCI) desorption curves of the MgH$_2$–Ni/Ti (Ni/Ti = 4/1) sample at different temperatures. The inset shows the van’t Hoff plot derived from the PCI curves.
The inset in Fig. 3.5 shows the corresponding van’t Hoff plot for the MgH$_2$–Ni/Ti (Ni/Ti = 4/1) sample based on the plateau pressures and the isothermal temperatures. The $\Delta H$ and the $\Delta S$ for this sample were calculated to be $67.8 \pm 0.1 \text{ kJ mol}^{-1}$ and $128.3 \pm 0.2 \text{ J mol}^{-1}\text{K}^{-1}$, respectively. The $T_{\text{des}}$ at 1 atm was then calculated to be 256 °C using Eq. 2.3 in Chapter 2, which is 22 °C lower than that of the pure MgH$_2$ sample.

The values of $\Delta H$, $\Delta S$, and $T_{\text{des}}$ for the other Ti- and Ni/Ti-catalyzed MgH$_2$ samples are also listed in Table 3.1. It can be seen from Table 3.1 that the samples doped with Ti and Ni/Ti have lower values of $\Delta H$, $\Delta S$, and $T_{\text{des}}$ compared with those of pure MgH$_2$.

It is also interesting to note that the combination of Ni and Ti improves the thermodynamic properties of MgH$_2$ significantly better than Ti alone. The Ni/Ti-catalyzed samples have two different molar ratios, i.e. Ni:Ti of 1:1 and Ni:Ti of 4:1. The Ni-rich sample exhibits a much lower desorption temperature, as evidenced from Table 3.1.

### 3.3.3.3 Kinetic measurements

**A. Desorption time**

The hydrogen desorption time, $t_{\text{release}}$ of the samples was evaluated using the volumetric method at 300 °C and a hydrogen pressure of 0.5 atm in terms of $\alpha$, the ‘reacted fraction’ as a function of time. Fig. 3.6 compares the temporal kinetic curves for all the samples. The pure MgH$_2$ sample took 46 min to release 80% of its total hydrogen content. The addition of 1 at.% Ti was found to reduce the desorption time to 652 s. The MgH$_2$–5 at.% Ti sample had a desorption time of 384 s. The desorption time of MgH$_2$ was reduced significantly when Ni and Ti were added together. The MgH$_2$–Ni/Ti (1:1) and MgH$_2$–Ni/Ti (4:1) samples have desorption times of only 28 s and 18 s, respectively.
Fig. 3.6 The hydrogen desorption time, $t_{\text{release}}$, of the pure and catalyzed MgH$_2$ at 300 °C and under a hydrogen pressure of 0.5 atm.

**B. Activation energy**

The activation energy, $E_A$, for the hydrogen desorption process of the samples was obtained from DSC measurements performed at different heating rates and by applying the Kissinger equation as discussed in Chapter 2:

$$\ln(\beta / T_p^2) = -\frac{E_A}{RT_p}$$

(3.2)

where $\beta$ is the heating rate, $T_p$ is the peak temperature, and $R$ is the universal gas constant. Fig. 3.7 shows the DSC curves of the MgH$_2$-1 at.% Ti sample at heating rates of 5, 10, 15, 20, and 30 °C min$^{-1}$. It is clear that the $T_p$ shifts to higher values as the heating rate $\beta$ increases. The $E_A$ value was calculated from the slope of the plot of $\ln(\beta / T_p^2)$ vs. 1000/$T_p$ as shown in the Fig. 3.7 inset. The same experiment was
repeated for the remaining samples to obtain the value of $E_A$, and they are tabulated in Table 3.1.

The decreasing trend in the $E_A$ values is in good agreement with the hydrogen desorption time curves obtained in Fig. 3.6. As can be seen from Table 3.1, the addition of 1 at.% Ti decreases the activation energy $E_A$ of MgH$_2$ from 249 kJ·mol$^{-1}$ to 205 kJ·mol$^{-1}$. Further addition of Ti leads to a further decrease in $E_A$ to 156 kJ·mol$^{-1}$. The samples with Ni/Ti show significant reductions in $E_A$. The samples with the Ni:Ti ratios of 1:1 and 4:1 have $E_A$ values of only 111 kJ·mol$^{-1}$ and 81 kJ·mol$^{-1}$, respectively. A plausible reason as to why the $E_A$ values of our samples are generally higher than those reported in the literature is because we are using low energy ball-milling equipment. However, it is sufficient to demonstrate the effects of Ni–Ti on the hydrogen desorption property of MgH$_2$. 
Fig. 3.7 DSC curves of the MgH$_2$–1 at.% Ti sample at heating rates of 5, 10, 15, 20, and 30 °C min$^{-1}$. The inset shows the Kissinger plot used to determine the activation energy.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$H_{\text{cap}} \pm 0.2$ (wt%)</th>
<th>$\Delta H \pm 0.1$ (kJ mol$^{-1}$)</th>
<th>$\Delta S \pm 0.2$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$T_{\text{des}} \pm 1$ (°C)</th>
<th>$E_a \pm 2.5$ (kJ mol$^{-1}$)</th>
<th>$t_{\text{release}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure MgH$_2$</td>
<td>4.9</td>
<td>76.7</td>
<td>139.2</td>
<td>278</td>
<td>250</td>
<td>2760</td>
</tr>
<tr>
<td>MgH$_2$ – 1 at.% Ti</td>
<td>4.9</td>
<td>76.2</td>
<td>138.4</td>
<td>278</td>
<td>208</td>
<td>652</td>
</tr>
<tr>
<td>MgH$_2$ – 5 at.% Ti</td>
<td>4.5</td>
<td>75.6</td>
<td>137.0</td>
<td>274</td>
<td>156</td>
<td>384</td>
</tr>
<tr>
<td>MgH$_2$ – Ni/Ti (1:1)</td>
<td>2.9</td>
<td>72.3</td>
<td>134.7</td>
<td>265</td>
<td>111</td>
<td>28</td>
</tr>
<tr>
<td>MgH$_2$ – Ni/Ti (4:1)</td>
<td>2.9</td>
<td>67.8</td>
<td>128.3</td>
<td>256</td>
<td>81</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 3.1 Summary of the hydrogen desorption performance of MgH$_2$ with different additives in terms of the hydrogen capacity, enthalpy, entropy, desorption temperature, activation energy, and desorption time (80% completion).

### 3.4 Synergistic effect of catalysts

Experimental work in this chapter clearly showed the presence of the synergistic effect of the Ni and Ti. The exact mechanism for the synergistic effect of the catalysts is of paramount importance in reducing the desorption temperature of the MgH$_2$ as well as
other promising hydrides. Efforts to understand the general synergistic effect of catalysts is, unfortunately, still very much at its infancy and only study on mixed additives of iron (Fe) and Zirconium (Zr) has been reported [16]. Consistent with the experimental results in this chapter, the mixed Fe and Zr additives resulted in faster hydrogen desorption kinetics than single additive. Ref. 16 explained the improvement in the desorption kinetics of the composite materials by assuming that the interfaces between the MgH$_2$ matrix and the transition metal nanoclusters act as heterogeneous sites for the nucleation of the Mg phase in the MgH$_2$ matrix and lead to the formation of fast diffusion channels for hydrogen migrating atoms.

3.5 Conclusions

Ti and Ni/Ti additives have been found to improve the desorption performance of MgH$_2$ in terms of the kinetics and the desorption temperature. From Table 3.1, the hydrogen desorption time, $t_{\text{release}}$, was shortened from 2760 s for the pure ball-milled MgH$_2$ down to a mere 18 s for one of the ball-milled samples with the Ni/Ti (Ni/Ti = 4/1) additive, which represents an improvement of 150 times. On the other hand, the same combination of additive only led to a 11.6% reduction in the enthalpy of hydrogen desorption. Subsequent chapters of this thesis cover some possible ways to improve the $\Delta H$ of MgH$_2$ (and hence the $T_{\text{des}}$), given the promise of MgH$_2$ as a hydrogen storage material for lightweight vehicles. Work based on first-principles calculations is also currently underway to study the Ni-Ti catalysis system in view of its seemingly intriguing synergetic effect.
3.6 References


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CHAPTER 4

Optical characterization technique

for MgH₂ powder

In this chapter, the proof-of-principle that interaction between visible light and a magnesium hydride sample in reflective mode can be used to determine the desorption temperature and kinetics of magnesium hydride in powder form is demonstrated. The demonstrated optical technique requires only milligrams of sample and can potentially be used to measure the de/absorption temperature and kinetics of magnesium nanostructures, which are often fabricated via the physical vapor deposition method inside an optically transparent quartz tube. This would help to eliminate the common problem of oxidation associated with removal and transport of the freshly fabricated nanostructures into an inert protective environment. This optical technique could be applied to any hydrogen storage material in the form of powder which shows a significant difference in its optical absorption between the hydride and the non-hydride phase.
4.1 Introduction

Hydrogen is seen by many as an environmentally friendly energy carrier to replace fossil fuels. Practical and successful use of hydrogen in transportation, however, requires hydrogen storage materials that can exhibit good reversibility and kinetics [1–3]. The desired temperature range at which the storage material releases its hydrogen content (known as the desorption temperature) is between 50°C and 100°C at 1 atm [1,3,4].

Magnesium (Mg) is one of the most promising hydrogen storage materials. It has a theoretical hydrogen uptake capacity of 7.6 wt%. Despite its high desorption temperature of about 300°C at 1 atm [1,3,5], research on magnesium is still ongoing in an attempt to significantly reduce the desorption temperature. This is because of its other advantages of good reversibility, low level of toxicity, and low cost [6,7].

The common techniques used to characterize the performance of hydrogen storage materials are volumetry, gravimetry, and differential scanning calorimetry (DSC) [1,8,9].

Hydrogen-storage materials have occasionally been prepared in the form of thin-films. Apart from the volumetric method and the differential scanning calorimetry (DSC) technique, the hydrogen storage properties of thin-films have been characterized using x-ray diffractometry [10,11], electrical resistance measurements [12–14], and optical methods [13–15].

An optical characterization technique known as hydrogenography has proved to be an efficient technique to determine the thermodynamics and kinetics of hydrogen de/absorption in thin metal films [16,17]. This technique is particularly efficient for
finding the optimum combinations of alloys, and it operates primarily in transmission mode.

A majority of hydrogen storage materials, including magnesium hydride, are, however, commonly synthesized by powder processing techniques such as ball milling. Therefore, we herein investigate and demonstrate the proof-of-principle that optical reflection from a powder sample of magnesium hydride (MgH$_2$) illuminated with visible light can potentially be used to characterize the hydrogen storage properties of the hydride, such as the desorption temperature and the kinetics of hydrogen release.

### 4.2 Some fundamentals of digital image processing

Before we go further, let’s look at some fundamentals of image processing relevant to this work. A grey-scale digital image is a two-dimensional array of integer numbers, in which each element of the matrix corresponds to a single pixel in the displayed image. The word *pixel* is derived from the phase “picture element”. For example, if an image consists of 100 rows and 200 columns of different colored pixels, the image can be expressed as a 100-by-200 matrix.

Some images, such as truecolor images, require a three-dimensional array, where the first plane in the third dimension represents the red pixel intensities, the second plane represents the green pixel intensities, and the third plane represents the blue pixel intensities. In other words, a truecolor image is an image in which each pixel is specified by three values, i.e., one each for the red, green and blue components of the pixel's color. The color of each pixel is then determined by the combination of the red (R), green (G), and blue (B) intensities stored in each color plane at the pixel's location.
Graphics file formats store truecolor images as 24-bit images, where the R, G, and B components each has an intensity level of 8-bits or $2^8$ steps. This yields a potential of 16 million colors. The precision with which a real-life image can be represented by this approach has led to the commonly used term of “truecolor” image. A truecolor image is also known as an RGB image.

Fig. 4.1 An example of a 24-bit truecolor digital image.

Fig. 4.1 shows an example of a truecolor image which consists of three planes of color, namely the red, green, and blue, each with an intensity level from 0 to 255. The fuselage of the model helicopter and the greenery in the background appear darker in the blue intensity image because the blue component in those regions is relatively low. The
intensity values of a typical pixel on the model helicopter fuselage are red: 216, green: 164, and blue: 29, as shown on the right side of Fig. 4.1. On the other hands, the blue sky appears much brighter in the blue intensity image than in the red intensity image.

4.3 Modeling of optical properties

To gain a better understanding of the optical properties of Mg and MgH₂, first principles calculations were performed to predict the change in the optical absorption between Mg and MgH₂, using the CASTEP module in Materials Studio [18] based on the Kramers-Kronig relations. The exchange-correlation functional used for the modelling of the crystal structures was the generalized gradient approximation (GGA), and the calculation was set up for normal incident angle and assuming bulk crystalline materials.

4.4 Experimental details

4.4.1 Preliminary experiment

A preliminary experiment was performed to determine if the transformation between MgH₂ and Mg has the required optical contrast for optical detection. About 30 mg of MgH₂ powder was spread thinly and evenly on a stainless steel substrate and heated up in a tube furnace to 450°C, with an argon flow rate of 200 mL min⁻¹ to prevent oxidation. The heat ramp used was 10°C per minute. Fluorescent lamps were used as the light source. Images of the sample were taken before and after heat-treatment with a charge-coupled device (CCD) camera. The images were taken under the same ambient lighting conditions.
4.4.2 Main experiment

4.4.2.1 Setup

Fig. 4.2 shows a schematic diagram of the experimental setup. A basic 240 V, 40 W soldering iron served as a microheater, which was compact enough to be housed inside the quartz tube and could provide the required heat to release hydrogen from the MgH$_2$ sample. The other main components of the setup were an RGB 320 × 240 pixel complementary metal-oxide semiconductor (CMOS) imager (webcam), and a quartz tube 1 m in length and with an inner diameter of 5 cm. A sample mass of about 7 mg was dispersed as thinly and evenly as possible on the top surface of the soldering iron using a spatula. The region of the soldering iron on which the sample was placed was carefully chosen so that variation in surface temperature was minimized. This ensured that heating across the sample area was as uniform as possible. Silicone tubing was used to channel argon gas into and out of the quartz tube, and both ends of the quartz tube were sealed using plastic wrap film and secured with tape.

![Schematic diagram of the experimental setup.](image)

The quartz tube was flushed with argon (flow rate of ~10 L min$^{-1}$) for 30 minutes before the start of the experiment. The flow rate during the experiment was approximately 0.5 L min$^{-1}$. The CMOS imager was placed above the magnesium sample outside the quartz tube, tilted at about 30$^\circ$ to the normal. The off-centered configuration was necessary to
prevent damage or undesirable thermal effects on the CMOS imager as a result of the heat dissipation from the heater. The light source was a blue light-emitting-diode with a peak wavelength of 470 nm.

### 4.4.2.2 Detection algorithm

The imager was connected to a laptop computer and the image processing was done in MATLAB using the MATLAB Image Processing Toolbox.

Only the region within the sample area in the acquired images was used for image processing. The acquisition frequency was 5 frames (data points) per second. The image has $320 \times 240$ pixels in RGB layers, each with a varying intensity level from 0 to 255. A suitable region of interest (ROI) for optical detection would be one in which the powder sample fully covers the supporting substrate. The size and position of the ROI can be software configured if necessary in order to select the suitable region of the sample for optimum optical detection.

The algorithm integrates the pixel intensity values enclosed within the selected region. In other words, the individual pixels collectively function as a single gigantic piece of detector that detects the optical differences in the sample as it undergoes the transition from MgH$_2$ to Mg. With this algorithm, the kinetics of hydrogen desorption of the sample, at temperatures above the desorption temperature, can be modeled as a kind of “population dynamics”, a term which we have borrowed from the field of ecology. The sample is virtually partitioned into discrete regions, with each of these partitions occupying/corresponding to a pixel on the imager. At any given time, at a sample temperature above the desorption temperature, a pixelated region with its corresponding optical intensity has a certain probability of registering the transformation from MgH$_2$ to
Mg. A pixel on the image was calculated to represent an estimated area of $200 \times 200 \mu m^2$ on the actual sample, based on the field-of-view of the imaging system, the resolution, and the distance between the imager and the sample.

The change in optical intensity resulting from the transformation of MgH$_2$ into Mg can then be represented by the “absorption fraction”, $\alpha$, which is equivalent to the “reaction fraction” $\alpha$ commonly used in hydrogen ab/desorption kinetic measurements performed using the volumetric method.

### 4.4.2.3 Experimental demonstration

Two different powder samples, namely MgH$_2$ and MgH$_2$ with 10wt% nickel nanopowder were used to demonstrate the proof of principle. The hydrogen-storage grade MgH$_2$ powder was purchased from Sigma-Aldrich (product number 683043). The sample with 10wt% nickel nanopowder was ball milled under argon for 1 hour with a ball-to-powder mass ratio of 25:1. The rotational speed was 400 rpm. The nickel nanopowder has an average particle size of less than 100 nm and was purchased from Sigma-Aldrich (product number 577995).

The phases of the pure MgH$_2$ samples before and after heating were verified by X-ray diffraction (with a step size of 0.02° and a scanning rate of 2° min$^{-1}$) using a GBC MMA diffractometer with Cu-K$\alpha$ radiation ($\lambda = 0.15405$ nm). Search-and-matches were performed using the software Traces from GBC with the International Center for Diffraction Data (ICDD) databases.

The temperature profile of the soldering iron on which the sample was positioned was measured separately as a function of time using a K-type thermocouple.
Dehydrogenation measurements by the volumetric method (Advanced Materials Corporation, U.S.) were performed for the MgH$_2$ and MgH$_2$ with nickel nanopowder samples so as to provide a meaningful basis for comparison with the results obtained from the optical technique. The mass of each sample loaded into the sample chamber was about 300 mg. Dehydrogenation was performed in 0.5 atm of hydrogen pressure, and the temperature was programmed to increase progressively to about 450°C.

The kinetics of hydrogen release was further quantified based on measurements of the activation energy, $E_a$, of the samples using a differential scanning calorimeter (DSC) from Mettler Toledo and the Kissinger equation. The argon flow rate was 25 mL min$^{-1}$.

### 4.5 Results and discussion

#### 4.5.1 Absorption coefficients

First principles calculation results for the absorption coefficients is as shown in Fig. 4.3, which predicts that Mg would have a much higher optical absorption than MgH$_2$ in the visible range (400 to 800 nm).

![Absorption Coefficient](image)

**Fig. 4.3** Results of first principles calculations used to predict the optical absorption coefficient.
4.5.2 Image analysis

Image analysis based on histograms for the individual colors in the images that were acquired during the preliminary experiment showed that the sample indeed exhibited observable optical contrast during the insulator-metal phase transition. The analysis also suggested that blue seems to have a slightly greater contrast than the other two colors, and therefore, the subsequent image processing was configured to acquire and process the optical intensity data in the blue. Fig. 4.4(a) shows the image histogram (blue intensity) of the MgH$_2$ powder sample with a mean intensity value of around 220. When the sample temperature has reached the desorption temperature, dehydrogenation begins to take place, and the sample powder is gradually transformed into Mg. Fig. 4.4(b) shows the image histogram of the Mg powder after the dehydrogenation has been completed, and its mean intensity value has been reduced to about 150, which represents a reduction of about 30%.
Fig. 4.4 Blue intensity image histogram for (a) the as-purchased MgH$_2$ powder sample and (b) the sample after the MgH$_2$ powder has been transformed into Mg.
4.5.3 Measurements by the standard volumetric method

Fig. 4.5 shows the variation in the absorbed fraction $\alpha$ as a function of time for the samples of as-purchased MgH$_2$ and MgH$_2$ with 10wt% Ni nanopowder, which was obtained using the volumetric method. The temperature profile has been included on the right-hand y-axis for ease of reference. The pure MgH$_2$ and the MgH$_2$ with 10wt% Ni began to release their hydrogen contents around 360°C and 240°C, respectively, which is consistent with the literature [1,3,5]. The desorption pressure was 0.5 atm.

![Graph showing absorbed fraction versus time](image)

Fig. 4.5 Desorption characteristics of the powder samples measured by the well-established volumetric method: (a) MgH$_2$ ball milled for 1 hour with 10 wt% nanopowder Ni, and (b) the as-purchased MgH$_2$. The pink curve shows the temperature evolution (right-hand y-axis) with time during the desorption.

4.5.4 Measurements by the proposed optical method

Fig. 4.6 shows the absorbed fraction $\alpha$ derived from the differences in the optical intensity values between the two samples, which have been integrated over all pixels within the sample region in the image as a function of time. The soldering iron was
energized at time $t = 0$ minutes. Curves 6(a) and (b) are for the MgH$_2$ and the MgH$_2$ with 10 wt% Ni nanopowder, respectively. The temperature evolution is also included in Fig. 4.6. The estimated uncertainty in the determination of the desorption temperature is $\pm 5^\circ$C, arising mainly from the fluctuation in the optical signal. The uncertainty in the temporal kinetic measurements was estimated to be $\pm 5$ s. Both samples desorbed at slightly higher temperatures relative to those obtained from the volumetric method, and this is expected, given that the ambient pressure was 1 atm instead of 0.5 atm. MgH$_2$ with nickel released its hydrogen content faster than the pure sample, and this is consistent with the fact that the former might have a lower activation energy of desorption. DSC measurements (Fig. 4.7) indeed yielded an $E_a$ value of 105 (±10) kJmol$^{-1}$ H$_2$ for MgH$_2$ with 10 wt% Ni, which was significantly lower than the $E_a$ for pure MgH$_2$ (~300 kJmol$^{-1}$ H$_2$) [19]. The heating rates were 10°C min$^{-1}$, 20°C min$^{-1}$, and 40°C min$^{-1}$.

![Fig. 4.6 Desorption characteristics of powder samples measured by the optical method in reflective mode: (a) MgH$_2$ ball-milled for 1 hour with 10 wt% nanopowder Ni, and (b) the as-purchased MgH$_2$. The light brown curve shows the temperature evolution, as indicated on the right-hand y-axis.](image-url)
There was minor oxidation that occurred after the dehydrogenation process, and this was probably due to the imperfect inert atmosphere inside the quartz tube. As a consequence, the optical intensity (and hence $\alpha$) increased slightly after the hydrogen had been released (Fig. 4.6). Nevertheless, we believe that the results provide a proof-of-principle that interaction between visible light and an MgH$_2$ powder sample in reflective mode can potentially be used to determine the desorption temperature and kinetics of the hydride.

4.5.5 Phase verification via X-ray diffraction

Figs. 4.8(a) and (b) shows the X-ray diffraction patterns for the as-received MgH$_2$ sample before and after the experiment, respectively. The results confirmed that the sample was initially magnesium hydride, but after the heat treatment, it was transformed into magnesium and some fraction of magnesium oxide (MgO). The X-ray diffraction
pattern in Fig. 4.8(a) was matched against ICDD database file number 72-1687 for MgH$_2$.

The relatively straightforward optical characterization method demonstrated herein requires only a few milligrams of sample material and is therefore particularly useful for samples that are only available in small quantity. Calculations based on the reactive force field approach and density functional theory (DFT) consistently suggest that nanostructures of magnesium, e.g. nanowires or nanodots, hold real promise for an improved desorption temperature for magnesium hydride [20,21]. A major hurdle confronting research and development on nanoscale materials for hydrogen storage is often the problem of oxidation.

The demonstrated optical technique can potentially be used to measure the de/absorption temperature and kinetics of magnesium nanostructures, which are often fabricated via the physical vapor deposition (PVD) method [22,23] inside an optically transparent quartz tube. This eliminates the problem of oxidation associated with removal and transport of the freshly fabricated nanostructures into an inert protective environment. Examples of magnesium-based structures fabricated in our laboratory using the PVD method can be found in the Appendix.
Fig. 4.8 X-ray diffraction patterns for (a) the as-received MgH$_2$ sample before the experiment and (b) the as-received MgH$_2$ sample after the experiment.

This optical technique could potentially be applied to any hydrogen storage material that shows a significant difference in the optical absorption between the hydride and the non-hydride phase, or in a more general sense, the transformation phases, such as in the case of complex hydrides, which often release hydrogen in multiple steps.

### 4.6 Conclusions

We have demonstrated that the desorption temperature and kinetics of magnesium hydride in powder form can be obtained from a relatively straightforward measurement of the change in light intensity reflected off the sample in the visible range. This optical technique can potentially be used to measure the de/absorption temperature and kinetics of magnesium nanostructures, which are often fabricated via the physical vapor deposition (PVD) method inside an optically transparent quartz tube. It can also be applied to other hydrogen storage materials in powder form that exhibit change in optical absorption during the de/hydrogenation process. Future work will involve
building an optical cell that can withstand hydrogen pressure up to approximately 20 atm and replacing the basic soldering iron with a proper temperature-controlled microheater. We hope that the new setup will enable us to investigate the ability of the optical system to measure the kinetics of ab/desorption of suitable hydrides at fixed temperature by varying the pressure of the cell and to generate pressure-composition-isotherm (PCI) curves.

4.7 References


CHAPTER 5

Magnesium thin film

In the previous chapter, the magnesium was synthesized by ball-milling which is a top-down approach. In this chapter, we fabricated Mg in the form of thin film, which is bottom-up approach. An 11 nm magnesium thin film capped with 2 nm palladium was deposited using the pulsed laser deposition technique. Its hydrogen de/absorption kinetics at room temperature was measured and found to have reached 80% completion within 5 minutes at 25°C. Raman spectroscopy reveals a small but detectable peak arising from the $E_g$ phonon mode of the magnesium hydride film, and the Raman frequencies of bulk magnesium hydride predicted by CASTEP calculations are included for comparison.
5.1 Introduction

Hydrogen storage materials that can exhibit reversible hydrogen de/absorption and fast kinetics would have important and useful applications in science and engineering [1,2,3]. Magnesium (Mg) is one of the most promising hydrogen storage materials, as it has a theoretical hydrogen uptake capacity of 7.6 wt%. Furthermore, it is known to have good reversibility, a low level of toxicity to the environment, and low cost because its ore is abundant in nature [4,5]. A major disadvantage, however, is that the hydride of magnesium (MgH₂) in the bulk form releases hydrogen slowly (i.e. slow kinetics of hydrogen desorption). It also has a rather stable hydrogen desorption enthalpy, \( \Delta H_{\text{des}} \), of approximately 75 kJ mol\(^{-1}\) H\(_2\), directly resulting in a temperature of hydrogen desorption, \( T_{\text{des}} \), of about 350°C at 1 atm [1,3,6], which would be inefficient for practical mobile applications such as energy storage in hydrogen-powered vehicles. An ideal hydrogen storage medium should be able to release its hydrogen content in the range of 25°C to 100°C [1,3,7]. Given the advantages of MgH₂, it is not surprising that there are ongoing research efforts to significantly reduce the desorption temperature and improve its kinetics.

Besides being considered as a hydrogen storage medium for mobile applications, magnesium in the form of thin film has other numerous potential applications, such as switchable mirrors for smart windows [8,9,10] and hydrogen gas sensing [11,12].

First principles calculations (FPC) have recently been carried out on magnesium nanowires to gain greater insight into the behavior of magnesium on the nanoscale, and the results indicated that nanowires 1.24 nm and 0.85 nm in diameter would have a reduced desorption enthalpy of 61.86 kJ mol\(^{-1}\) H\(_2\) and 34.54 kJ mol\(^{-1}\) H\(_2\), respectively [13]. A similar study with consistent results has been performed on magnesium and
magnesium hydride systems based on the reactive force field (ReaxFF\textsubscript{MgH}) [14]. Based on the theoretical predictions, thin film having thickness of 3 nm and above is not expected to yield significant nano-confinement effect and hence the reduction in the desorption temperature.

Magnesium in the form of thin film would serve as an invaluable one-dimensional quantum system to investigate the fundamental properties of hydrogen de/adsorption behavior in the ultra-low nanometric range. This is because films close to the desired thickness can be fabricated by controlling the deposition time, once the rate of deposition has been established, while keeping other deposition parameters such as the sputtering power and base pressure constant, as in the case of film deposition by magnetron sputtering.

Although considerable research has been done on magnesium thin film, we would like to point out that most magnesium-based thin films characterized for their hydrogen de/adsorption properties had been fabricated using magnetron sputtering [8–12,15–18]. Other fabrication techniques used include electron beam physical vapor deposition [19] and thermal evaporation [20]. These magnesium-based thin films often have film thicknesses of 40 nm and above [8–12,16–20]. In Ref. [15], a magnetron sputtered Mg film having a thickness of 10 nm was investigated, but the thickness of the Pd capping layer was 40 nm and there was no explicit kinetic characterization as a function of time. Singh et al. [21] and Bouhtiyya et al. [22] investigated magnesium-based thin films produced by pulsed laser deposition, but the Mg film thicknesses were 1 \textmu m and 170 nm, respectively. Given that magnesium nanostructures in the ultra-low nanometric range should exhibit markedly improved hydrogen desorption along with a significant increase in the kinetics as compared with their bulk counterpart, we herein fabricate an
11 nm magnesium ultrathin film capped with only 2 nm palladium (Pd). The film was deposited on glass substrate by pulsed laser deposition, in an attempt to investigate / characterize the hydrogen de/absorption properties of magnesium thin films in the ultra-low nanometric range (ultrathin film) in air and at 25 °C. The purpose of the 2 nm Pd capping layer in this work was to prevent oxidation of the Mg film, although it will inevitably promote molecular hydrogen dissociation during the absorption stage [11]. Kinetics of hydrogen absorption and release of the ultrathin film are compared to those of thicker Mg thin films 30 and 200 nm in thickness.

5.2 Experimental details

5.2.1 Film deposition

The Pd-Mg films were prepared by pulsed-laser deposition at room temperature using a krypton fluoride gas laser (\(\lambda = 248\) nm). The metallic films were deposited on glass substrates with dimensions of 1 cm \(\times\) 1 cm. The vacuum base pressure used for deposition was around \(6 \times 10^{-7}\) Torr. The laser pulse output frequency was 10 Hz, and the energy per pulse was 550 (\(\pm 3\)) mJ. The purity of the Mg and Pd targets was 99.9% and 99.95%, respectively. Pre-deposition processing was performed by irradiating the targets with 5 Hz laser pulses for 15 s to remove any possible surface contaminants such as oxides prior to the actual deposition. During the target pre-deposition process the glass substrate was positioned away from the plasma plume region to avoid any undesirable deposition on the glass substrate. The deposition rates of Mg and Pd were established as 0.333 nm s\(^{-1}\) and 0.143 nm s\(^{-1}\), respectively. Other Mg films 30 and 200 nm in thickness were fabricated for comparison purposes. They were similarly capped
with 2 nm Pd. The thickness of films was measured using a stylus profilometer within an accuracy of ± 1 nm.

5.2.2 Optical measurements

Optical measurements of the thin films were performed in transmissive mode though the glass windows in a gas-sealed optical cell. A diffused blue light emitting diode (LED; λ = 470 nm) with a collimating lens was used as the light source, and the imaging/detection system consisted of a complementary metal-oxide-semiconductor (CMOS) imager with a resolution of 320 × 240 pixels. The image acquisition and processing were performed in MATLAB®, using the MATLAB® Image Acquisition Toolbox and Image Processing Toolbox.

Magnesium is a metal, and so it strongly attenuates incident light. On the other hand, magnesium hydride is an insulator which allows most visible light to pass through it, and so it appears to be semi-transparent. Therefore, when a piece of magnesium film is undergoing hydrogen absorption, the transition from magnesium to magnesium hydride will cause the film to change from a more opaque state to a more transparent state. The change in the amount of light transmitted through the film can therefore be used to monitor the progress of the hydrogen absorption of the film, or the kinetics of absorption, if the progress is monitored as a function of time.

The Beer-Lambert law dictates that the hydrogen concentration in a film during absorption, \( c_{\text{H}} \), is proportional to the logarithm of the optical intensity of the transmitted light through the film, \( T \), normalized to the intensity of the transmitted light when the film is in the metallic state, \( T_0 \) [18]. In other words, \( c_{\text{H}} \propto \ln(T/T_0) \).
The hydrogen absorption fraction or the so called “reacted fraction”, $\alpha$, as commonly encountered in the volumetric characterization method, could then be expressed as the concentration of hydrogen at a given time, $c_H$, divided by the final concentration of hydrogen, $c_{H\text{ final}}$, that is $\alpha = \frac{c_H}{c_{H\text{ final}}}$. This expression is useful, especially in the study of kinetics.

### 5.2.3 Hydrogen de/absorption kinetics

The films were soaked in hydrogen inside an optical cell at 0.25 atm and at 25°C. The absorption pressure of 0.25 atm was chosen because magnesium thin film can readily absorb hydrogen gas to form MgH$_2$ and 0.25 atm is about the lowest the pressure transducer can reliably measure before the measurement error gets too large. The optical cell was connected to commercial Sieverts apparatus from the Advanced Materials Corporation. The optical cell was evacuated prior to hydrogenation. The initial hydrogen pressure in the reservoir was set such that when the gas valve separating the reservoir and the optical cell was opened, the final hydrogen pressure in the optical cell would reach an equilibrium value of 0.25 atm. Kinetics of hydrogen absorption by the films was recorded by monitoring the change in optical intensity of the film in real time in the presence of hydrogen.

During the transition from hydrogen absorption to hydrogen desorption, an air valve in the optical cell was actuated to allow air to enter the optical cell, and the pressure inside the cell was then equilibrated to 1 atm. The optical signal was recorded and processed in the same manner as in the absorption test.
X-ray diffraction (XRD, Cu Kα) was used to verify the phases and any possible preference in the growth orientation of the film. The scanning rate was 1° per minute, and the step size was 0.02°.

The surface topography and roughness of the 11 nm Mg ultrathin film on glass were studied using an atomic force microscope (AFM) operating in the tapping mode. The AFM tip was silicon (Si) with a Si₃N₄ coating. The scan area was 2 × 2 µm with a scanning rate of 1 Hz, and the line scan resolution was set to 512. All the measurements were performed under ambient conditions. The surface roughness of the films was quantified by the root-mean-squared (rms) value.

Raman spectroscopy (HORIBA Jobin Yvon) was used to study the optical phonon modes of the ultrathin film. The Raman measurements were performed with the thin film enclosed inside the optical cell in a hydrogen atmosphere to ensure that it remained in the hydride state. The coherent excitation wavelength was 632.81 nm, and the grating used was 300 lines per mm. The accuracy associated with the Raman-shift measurement was ±1.5 cm⁻¹ (or ±0.186 meV). The instrument was calibrated prior to the actual measurements, and standard silicon with a known Raman peak at 520.7 cm⁻¹ was used to verify the accuracy of the calibration. Raman spectra were also acquired for a bulk MgH₂ powder sample from Sigma-Aldrich (product number 683043) for spectral comparison. It was necessary to acquire the spectrum for the ultrathin film using multiple runs because only a relatively small amount of the coherent radiation at normal incidence was being back scattered compared with the bulk sample, and only a fraction of the back scattered light carried the Raman signal from the ultrathin film, with the rest being the Rayleigh scattering.
Calculation of the Raman peak positions, as well as their relative intensities, for the bulk MgH$_2$ were performed using the Cambridge Sequential Total Energy Package (CASTEP) within Materials Studio based on the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [23]. The electron-ion interaction was represented by the norm-conserving pseudopotentials. Structural optimization was performed prior to the lattice dynamics calculations, and lattice parameters were converged to $2 \times 10^{-5}$ Å, as phonon calculations are sensitive to crystal structure. The self-consistent field (SCF) convergence criterion was set to $1 \times 10^{-8}$ eV per atom, and a k-point grid of $14 \times 14 \times 10$ was used. The Raman activity tensor of a given vibrational mode (frequency) was calculated using the derivative of the dielectric permittivity tensor with respect to the mode amplitude [24].

5.3 Results and discussion

5.3.1 Structural characterization

The x-ray diffraction pattern for the 11 nm ultrathin film did not yield any observable peaks related to magnesium. However, the x-ray diffraction pattern (Fig. 5.1) of a thicker 50 nm magnesium thin film fabricated by our pulsed laser deposition system did show a preferred growth orientation in the (002) direction, which is the same preferred orientation shown by Pd-Mg and other Mg-based thin films prepared by sputtering, thermal evaporation, and electron beam physical vapor deposition techniques [17–20]. The X-ray diffraction pattern shown in Fig. 5.1 was matched against the International Center for Diffraction Data (ICDD) database file number 35-821 for magnesium.
Fig. 5.1 X-ray diffraction pattern for a 50 nm film prepared by pulsed laser deposition reveals a strong preferred orientation in the (002) direction. The ICDD database pattern 35-821 for magnesium is also shown in the lower part of the plot.

Fig. 5.2(a) and (b) shows the AFM images for the 11 nm Mg film in 2D and 3D, respectively, which seem to suggest that the film morphology is dominated by island growth (Volmer-Weber). Similar film topography was obtained in ref. [25] by the pulsed-laser deposition technique and was referred to as having a nanoparticle-like appearance. The rms surface roughness of the Mg film was determined to be 0.916 nm.
Fig. 5.2 (a) AFM image of the 11 nm Mg ultrathin film on glass substrate in 2D, and (b) AFM image of the 11 nm Mg ultrathin film on glass substrate in 3D.

5.3.2 Hydrogen de/absorption kinetics

Fig. 5.3 shows the fraction of hydrogen absorption as a function of time for the 11, 30, and 200 nm magnesium thin films at 0.25 atm of hydrogen pressure and at 25°C. The 11 nm ultrathin film reached an absorption fraction of 80% in 3.3 minutes, while it took 14 minutes for the 30 nm film to reach the same absorption fraction. There was no observable absorption for the 200 nm magnesium film within a time frame of 25 minutes. Absorption kinetics for the 11 nm film at 0.75 atm H\textsubscript{2} pressure is also included.
in Fig. 5.3, which is faster (reaching 80% completion in 45 seconds) than the absorption at 0.25 atm, as would be expected.

Fig. 5.3 Hydrogen loading kinetics comparison at 0.25 atm hydrogen pressure and 25°C for films of different thicknesses. Hydrogen loading pressure of 0.75 atm for the 11 nm film is also included.

Fig. 5.4 shows the fraction of hydrogen desorption as a function of time for the thin films in air at 1 atm and 25°C. The 11 nm magnesium ultrathin film desorbed readily and released 80% of its hydrogen content in just 2.9 minutes.
There have been reports of the possibility of formation of Pd-Mg alloy, which might occur in the interface between the Mg and the Pd protective layer, particularly at elevated temperature, for example, 60°C and above [15,21]. It has been a significant challenge to directly detect the existence of the Pd-Mg alloy in metallic thin films, given the often extremely thin layer of the alloy. Fischer et al. detected the formation of Pd-Mg alloy as thin as three monolayers thick for Pd/Mg films deposited by evaporation [26]. Baldi et al. [15] was able to elegantly infer the existence of the Pd-Mg alloy from the plot of the plateau width (that is, the optical contrast between the metal and hydride states) against Mg film thickness by an optical method, and they noted that there was “missing” Mg thickness in the form of a positive x-axis intercept, when there should be no plateau width as the Mg thickness approaches zero. Given the fact that we have also observed the gradual reduction in the optical contrast during the hydrogen charging/discharging cycle of the film, we thus conclude that the reduction in the observed contrast is likely to be due to the gradual formation of Pd-Mg alloy in our thin
film samples along the Pd-Mg interface, as the metallic layers experienced lattice expansion and contraction during the hydrogen cycling process. An effective solution to the Pd-Mg alloy problem and the loss of optical contrast can be achieved by having a titanium (Ti) buffer layer, as demonstrated by Baldi et al. [15]. We opted for a simpler material system and did not incorporate the Ti buffer layer in this work, as our emphasis in this work was to quantitatively characterize the kinetics of the Mg films as a function of time and to study the possible changes in the lattice vibrations of the Mg film on the ultrathin, low nanometric scale. The Pd layer was primarily used as a protective layer to prevent the Mg film from oxidizing in this study.

5.3.3 Raman spectroscopy

Fig. 5.5 shows Raman spectra for both the as-purchased MgH$_2$ bulk powder sample and the hydrogenated 11 nm ultrathin film. The Raman spectrum for the bulk powder sample shows three main peaks centered around 314.9 cm$^{-1}$, 954 cm$^{-1}$, and 1276 cm$^{-1}$, corresponding to the Raman-active modes of vibrational symmetries $B_{1g}$, $E_g$, and $A_{1g}$, which is in good agreement with the experimental Raman measurements at room temperature reported by Santisteban et al. [27], with the peak around 954 cm$^{-1}$ ($E_g$ mode) being the most prominent. The equivalent peak values in units of electron-volts (eV) are also included in parentheses in Fig. 5.5. The calculated Raman peak positions as well as their relative intensities for the bulk MgH$_2$ were also consistent with the Raman spectra, and they are represented by the red bar graph in Fig. 5.5. The Raman mode frequencies predicted by CASTEP were 307.2 cm$^{-1}$ (38.1 meV), 953.5 cm$^{-1}$ (118.3 meV), and 1267.6 cm$^{-1}$ (157.3 meV) for the $B_{1g}$, $E_g$, and $A_{1g}$ peaks, respectively, and the discrepancies between the experimental and predicted values were well within
the acceptable value of 10 cm\(^{-1}\) that is typical for density functional theory (DFT) lattice dynamics calculations [24].

It has been found that wavenumbers higher than 450 cm\(^{-1}\) for MgH\(_2\) generally correspond to the hydrogen-related optical vibrations, and the broad widths of these peaks could suggest a large dispersion of the optical phonons, which implies the presence of strong hydrogen-hydrogen interactions [27]. Broad and relatively weaker peaks, such as those centered around 590.8 cm\(^{-1}\) and 1186 cm\(^{-1}\), are likely to originate from second-order processes, while the smaller and sharper peak at 441.4 cm\(^{-1}\) is likely to be attributable to first-order processes of Raman origin [27].

The Raman spectrum for the ultrathin film begins at 500 cm\(^{-1}\) because the signal-to-noise ratio in the lower wavenumber region was poor. This was due to the large background in the region because of proximity to the 0\(^{th}\) order of the excitation laser line of 632.81 nm.
Fig. 5.5 Raman spectra for the 11 nm film and the bulk powder sample, which cover the three main vibrational modes of bulk MgH$_2$ at room temperature, namely, the $B_{1g}$, $E_g$ and $A_{1g}$ modes. Raman peak positions and relative intensities predicted by CASTEP are represented by the red bar graph.

Fig. 5.6 Raman spectra for the 11 nm film and the bulk MgH$_2$ powder sample centered around the $E_g$ peak. Bulk Pd was included as a confirmation check to ensure that the observed peak was indeed a real Raman signal. No smoothing function or baseline corrections were applied to these vibrational data curves, so as to preserve the integrity of the peak information.
The prominent $E_g$ peak at 954 cm$^{-1}$ was studied in greater detail because the peak can be clearly distinguished in the ultrathin film spectrum and also because the optical phonon mode is relevant to the study of hydride. The magnitudes of the $E_g$ peaks from the 11 nm film and the bulk sample were equalized so as to facilitate peak profile comparison, as shown in Fig. 5.6. Bulk Pd, which does not have vibrational modes around the 950 cm$^{-1}$ region, was included to provide convincing evidence that the peak observed in the 11 nm thin film was indeed a Raman signal and not noise or anomaly arising from the equipment system. From Fig. 5.6, one could clearly see that there was no observable peak for the bulk Pd, as expected, whereas there was a small but observable Raman peak for the 11 nm Mg film around the 950 cm$^{-1}$ mode.

Note that no smoothing function or baseline corrections were applied to these vibrational data curves, so as to preserve the integrity of the peak information. The width of the peaks was measured in terms of the full width at half maximum height (FWHM). The results in Fig. 5.6 show that the peak from the 11 nm film was broadened and shifted to a lower wavenumber by 30 cm$^{-1}$ compared to the peak in the bulk sample. These changes are qualitatively consistent with the Raman results published on germanium, as it made the transition from bulk to nanocrystallite [28]. Similar trends have also been reported for silicon [29] and graphite [30]. While we are yet to firmly establish the link between the reduction in the Raman frequency and the hydrogen storage properties of the film, we think that a lowered vibrational frequency might imply a weakened Mg-H bond, which would translate into a lowered $T_{\text{des}}$. The reduction in $T_{\text{des}}$ as a function of Mg film thickness has been reported from thermodynamic measurements in Ref. [15]. The broadening of the peak, on the other hand, could imply a much stronger interaction among the hydrogen atoms in the 11 nm film than in the bulk.
Future work will be carried out to investigate the possible relationship between the Raman shift and the $T_{\text{des}}$, as well as the role of hydrogen-hydrogen interaction in MgH$_2$ ultrathin films, in greater detail. The understanding gained may help to effectively reduce the temperature of desorption of other promising hydrides as well.

5.4 Conclusions

We fabricated an 11 nm magnesium ultrathin film capped with 2 nm Pd. Optical transmission characterization of the film showed that it was capable of hydrogen de/absorption with 80% completion in about 3 minutes in air at 25°C. The hydrogen pressure during the absorption test was 0.25 atm. The desorption temperature in air was estimated to be 3°C using the van’t Hoff’s equation. Raman measurements showed shifting and broadening of the $E_g$ mode associated with strong hydrogen-hydrogen interaction within the hydride. Both the phonon calculations performed in CASTEP and the Raman measurement of the bulk MgH$_2$ at room temperature and pressure using the 632 nm excitation line are shown to be in good agreement with each other in terms of the vibrational Raman frequencies and the relative intensities, including the frequency of the main $E_g$ vibrational mode centered around 940 cm$^{-1}$. Magnesium thin film, which is capable of hydrogen de/absorption under ambient conditions with good kinetics, will certainly bring us a step closer to realizing its numerous potential room-temperature applications, such as hydrogen sensors, switchable mirrors for smart windows, and hydrogen storage for mobile applications.
5.5 References

CHAPTER 6

Multi-stacked structure for switching contrast enhancement of hydride-based switchable mirrors

Hydride-based switchable mirrors were reviewed along with their important applications, including hydrogen gas safety sensors and smart windows, in Chapter 2.

We here propose and demonstrate a multi-stacked structure intended for low-nanometer ultrathin films of various metal hydrides that would enable them to simultaneously achieve enhanced optical contrast equivalent to that of thicker film, while still retaining much of the rapid switching kinetics characteristic of low-nanometer ultrathin films. Such improvement in the performance will help to extend the scope of applications further, particularly in the area of dynamic switchable mirrors, where switching speed and high switching contrast are at a premium.

The demonstrated concept of a multi-stacked structure with nanometer spacing could also potentially be used to increase the effective volumetric hydrogen storage density of ultrathin films of promising hydrides for mobile applications, without adversely affecting the highly desirable kinetics and thermodynamics of these films.
6.1 Introduction

Hydrides in the form of thin films have received considerable interest in the development of important thin film devices such as hydrogen detectors, metal hydride switchable mirrors, and tunable magnetic elements, based on their unique optical properties, which strongly depend on hydrogen concentration [1–9]. In the U.S., about 30% of primary energy consumption is used for heating and cooling of residential and office buildings [10]. Smart coatings and switchable mirrors can play an important role in reducing the energy consumption of buildings and in transportation. The switchable mirrors can also be used as two-dimensional hydrogen concentration indicators in basic research [9].

The metallic thin films that exhibit significant changes in their optical properties when hydrogenated include films of palladium (Pd) [2,3], rare-earth metals such as yttrium (Y) and lanthanum (La) [11,12], and magnesium (Mg), and magnesium-based thin films such as those made from Mg2Ni [1,4–8]. Palladium (Pd) was reported to reversibly absorb hydrogen gas as far back as 1866 [13]. At room temperature and atmospheric pressure, palladium can absorb up to 900 times its own volume of hydrogen [14]. Pd is one of the most studied metals for hydrogen storage in terms of microstructural, thermodynamic, and kinetic properties. It is also a model system for hydrogen storage [15]. Pd has also been widely researched and utilized as a metallic membrane for hydrogen separation and purification, since it is highly permeable to hydrogen, resistant to ambient conditions of air, oxygen, and moisture, and can rapidly dissociate hydrogen molecules into atoms on its surface [16]. The prefactor of the diffusion coefficient, $D_0$, and the activation energy, $E_a$, for a 22.5 nm thick Pd thin film fabricated using physical
vapor deposition has been found to be $3.9 \times 10^{-5}$ cm$^2$ s$^{-1}$ and 36.3 kJ mol$^{-1}$, respectively, based on electrochemical method [17].

Applications in switchable mirrors and hydrogen gas sensing often demand high optical switching contrast, as well as short response time [4,9,18]. In general, the optical switching contrast of a thin film can be effectively enhanced by simply increasing the thickness of the film. However, when the thickness of the film is increased, the switching time becomes longer as well. For example, we fabricated an Mg ultrathin film 11 nm in thickness on glass substrate capped with 2 to 3 nm palladium using the pulsed laser deposition technique, as described in the previous chapter, and found that the ultrathin film could absorb and release 80% of its hydrogen content at room temperature in air at 0.25 atm in 3.3 minutes. The thicker 30 nm Mg film, on the contrary, took 14 minutes for hydrogen absorption, but the metal-to-insulator transition gave a much higher optical contrast than that of the 11 nm Mg thin film. The increase in switching contrast with film thickness is also apparent in ref. [7], in which it is related to the term $\ln(T/T_{M})$, where $T$ is the transmittance and $T_{M}$ the transmittance in the metallic state.

Given the significant merits and requirements for simultaneous fast optical switching (or response time) and high optical contrast, especially in applications of switchable mirrors such as smart windows, we herein propose and investigate a multi-stacked structure specifically applicable to ultrathin films that would yield the high optical contrast equivalent of a “thicker” film and yet retain much of the desirable fast switching speed often associated with ultrathin film.

Nanometer thick fullerene (C$_{60}$) was evaluated in this work for its suitability as a spacing layer that could provide physical support for the ultrathin film layers and allow
rapid hydrogen diffusion, so as to enable hydrogen loading and unloading of the stacked metal films. Pd was chosen as the active hydrogen absorbing film in this “proof-of-concept” experiment, given that it is a well researched hydrogen storage metal, and its relative stability under ambient conditions means that there is no need for a protective capping layer, so that we can focus more on the investigation of the novel characteristics of the multi-stacked structure rather than the hydrogenation properties of the active Pd layer. We expected that the proposed concept of a multi-stacked structure could be applied to any metal hydride system in the form of an ultrathin film, including the Mg based thin films. Two layers of 10 nm single layer Pd films were spaced by a layer of C\(_{60}\), giving a Pd-C\(_{60}\)-Pd structural configuration in this “proof-of-concept” experiment. The thickness of the C\(_{60}\) layer was varied to study its possible effects on the switching speed of the Pd-C\(_{60}\)-Pd multi-stacked structure. The final section of this paper reports on the determination of the hydrogen diffusion pathways in the multi-stacked film structure.

6.2 Experimental details

6.2.1 Film deposition

The Pd single layer and multi-stacked ultrathin film structures were deposited on glass substrates by thermal evaporation. The evaporator unit was housed inside a nitrogen filled glove box, as shown in Fig. 6.1. Its operation was controlled by a computer, and it has a built-in quartz thickness sensor with the capability to monitor the deposition rate and film thickness in real time. The evaporator was found to give good thickness uniformity for a deposition area of about 10 × 10 cm\(^2\), and therefore, batch fabrication
was used whenever necessary to make thin film samples with high consistency in terms of material properties within the same batch of films.

Fig. 6.1 The thermal evaporator used to fabricate the thin film structures was housed inside a nitrogen glove box. The evaporator has a built-in quartz thickness sensor, and the deposition process is computer controlled.

The active metallic area of the thin film samples deposited on glass was 8 mm × 15 mm. Batch fabrication allowed some film samples to be used as controls while others were used as the characterization samples to ensure reliability of the experimental results. The film thicknesses were further verified by profilometry to an accuracy of ±1 nm. The purity of the Pd target was 99.99%. The multi-stacked ultrathin film structures of Pd-C₆₀(ₓ)-Pd were fabricated based on sandwiching an interior C₆₀ layer of thickness, 𝑥, of 5 nm, 10 nm, and 20 nm between 10 nm Pd single layer thin films. The deposition of the Pd and the C₆₀ layers was carried out in a single session without breaking the chamber vacuum.
6.2.2 UV-Vis spectroscopy

The transmittance, $T$, of the freshly vacuum evaporated Pd thin films was measured using an ultraviolet-visible (UV-Vis) spectrometer. The transmittance of the multi-stacked film structures with various $C_{60}$ thicknesses was measured primarily to verify if the material of the sandwiched layer was indeed $C_{60}$. The calibration was performed on a glass substrate prior to measurement so as to minimize the effects of the glass substrate on the transmittance spectra of the Pd metal thin films. As the light propagates into a piece of metallic thin film, the light intensity, in general, decays as it propagates further into the thin film. If the metallic thin film has an absorption coefficient $\alpha$, then the intensity of light $I$ as it propagates $x$ distance into the thin film can be obtained from Lambert’s law [19]

$$I(x) = I_s \cdot e^{-\alpha x} \quad (6.1)$$

where $I_s$ is the intensity of light just before it enters the metallic thin film.

The absorption coefficient $\alpha$ of the film can be related to the extinction coefficient, $\kappa$, at a given incident wavelength, $\lambda$, as

$$a = \frac{4\pi \cdot \kappa}{\lambda} \quad (6.2)$$

Furthermore, Eq. (6.1) can be rearranged to obtain

$$\ln(T) = -\alpha \chi \quad (6.3)$$

where $T (= I / I_s)$ is the transmittance of the film at a given incident wavelength $\lambda$. 
UV-Vis spectroscopy was also used to confirm the identification of the vacuum evaporated C$_{60}$ thin film layers, as C$_{60}$ has a UV absorption peak around 350 nm. The C$_{60}$ film can be identified either by benchmarking against its own spectra or against that of [6,6]-phenyl-C$_{61}$-butyric acid methyl ester, commonly known as PCBM as it is a fullerene derivative of the C$_{60}$ [20].

6.2.3 Optical contrast and switching speed characterizations

For a metal film of constant thickness, the Beer-Lambert law dictates that the hydrogen concentration in the film during absorption, $c_H$, is proportional to the logarithm of the optical intensity of the transmitted light through the film, $I$, normalized to the intensity of the transmitted light when the film is in the metallic state, $I_M$ [21]. In other words, $c_H \propto \ln(I/I_M)$ for a given film. In this work, however, we would be more interested in the optical contrast of the thin film, and the contrast assumes the form of the expression for the Weber contrast, $(I - I_M)/I_M$, where $I_M$ is the measured intensity of the fresh metallic film, and $I$ is the measured intensity after the metal film has been soaked in hydrogen. When the film has been fully hydrogenated at a given hydrogen pressure, then the measured intensity at the detector becomes $I = I_H$.

The thin film sample to be characterized was housed inside a custom-designed hermetic optical cell, which was connected to a commercial Sieverts-type apparatus from the Advanced Materials Corporation. The role of the hydrogen testing machine was to administer the flow of hydrogen gas into and out of the optical cell, including cell pressure monitoring and evacuation of the cell. The optical measurement was performed in transmissive mode though a pair of glass windows on the optical cell. The light
source was a green light emitting diode (water clear lens, $\lambda = 530$ nm), and the light intensity after transmission through the thin film was measured using a Thorlabs PM100 optical power meter, and the slim S130A sensor that was attached directly onto the optical cell to ensure maximum detection stability. The optical power meter was connected to a computer for data acquisition via the RS-232 link, and the time interval between the data points was set to 0.25 s. We refer to the positive change in the transmittance of the films during hydrogen uptake as the “response” phase and the reduction in the transmittance of the films during hydrogen release as the “recovery” phase, so as to be consistent with the terminologies commonly used in hydrogen thin film sensor and switchable window research. The hydrogen pressure during the response phase was 0.3 atm, and the type of gas used during the recovery phase was air at a gas pressure of 0.8 atm. The response and recovery time were measured at 80% switching completion. All optical cell measurements were performed in the transmissive mode.

Fig. 6.2 shows the various film configurations used in this work, and they can be broadly divided into three categories, namely, the single Pd films (for example, 5, 10, and 23 nm), the multi-stacked film structures Pd-C$_{60}(x)$-Pd, and the dual 10 nm film. The dual 10 nm film consists of two samples of 10 nm Pd single layer film physically stacked together with a 1 to 2 mm gap between them.
Fig. 6.2 The various thin film configurations used to investigate the switching speed and optical contrast of the films. All measurements were performed in transmissive mode with incident wavelength of 530 nm.

### 6.2.4 Crystal structures and surface morphology

The crystalline structure of the single layer Pd films was characterized by x-ray diffraction (XRD) with a step size of 0.02° and a scanning rate of 1° min⁻¹, using a GBC MMA diffractometer with Cu-Kα radiation (λ = 0.15405 nm). Multiple scans were used for the Pd thin films to obtain satisfactory peak information, given the small amount of material available in the thin film samples. Search-and-matches were performed using the software package Traces from GBC with the International Center for Diffraction Data (ICDD) databases. The morphology and surface roughness of the Pd films deposited on glass were characterized using an atomic force microscope (AFM) operating in tapping mode. The AFM tip was silicon (Si) with a Si₃N₄ coating. The scan area was 1 × 1 µm. The scanning rate was 1 Hz and the line scan resolution was set to 512. All the measurements were performed under ambient conditions. The surface roughness of the films was quantified using the root-mean-square (rms) values.
6.2.5 Hydrogen diffusion pathway

An attempt was made to determine the hydrogen diffusion pathway in the multi-stacked Pd-C$_{60}$-Pd film structures based on the Pd-C$_{60}$(10nm)-Pd. In other words, we would like to determine if the hydrogen gas diffused into the stacked structure primarily via the top surface of the structure or though the edges of the structure. The samples were sealed with adhesive tape, and various seal configurations were applied to the samples to determine the likely hydrogen diffusion pathway into the multi-stacked Pd-C$_{60}$-Pd film structure, as shown in Fig. 6.3. The switching speeds were measured using the optical cell in 0.3 atm hydrogen pressure to obtain a relative switching speed comparison plot. Pd-C$_{60}$-Pd film structures from the same evaporation batch were used for this work whenever possible. A proper adhesive seal is essential, but excessive force should be avoided to prevent or minimize damage to the multi-stacked film structures.

A control test with the optical cell was performed on a sample with only adhesive tape applied onto the glass substrate to check if it would give measurable switching contrast when hydrogenated. The response time of the “As-it-is” (Asii) sample with no adhesive tape [Fig. 6.3(a)] was tested in the optical cell. The metallic film edges of the Asii sample were then sealed with adhesive tape to obtain the “Edge-sealed” (EdgS) sample [Fig. 6.3(b)], making sure that the adhesive tapes were placed outside the boundaries of the optical detection zone to ensure that the active area of the optical detection zone remained the same as in the Asii. The switching speed of the EdgS sample was again measured in the optical cell. A piece of adhesive tape slightly smaller than the area of the metal film was gently applied to an Asii sample to obtain the “Surface-sealed” (SurfS) sample [Fig. 6.3(c)] while leaving the edges of the film exposed, making sure that no exposed metallic Pd film area was within the boundary of the detection zone. The SurfS sample was converted into the “Completely-sealed” (ComS) sample [Fig.
6.3(d)] by simply applying a piece of adhesive tape covering the entire Pd film and glass substrate surface.

The Asii and the EdgS samples were extended to Pd-C$_{60}$-Pd film structures with C$_{60}$ film thicknesses of 20 nm and 60 nm to determine if the thickness of the C$_{60}$ layer within that range would make any difference to the hydrogen diffusion pathway via the edges of the film structures.

![Diagram showing various seal configurations](image)

**Fig. 6.3** Various seal configurations used to determine the hydrogen diffusion pathway of the multi-stacked structure.
6.3 Results and discussion

6.3.1 UV-Vis spectroscopy

6.3.1.1 Pd single layer thin films

Fig. 6.4. shows the results of the transmittance ($T$) measurements for the single layer thin films using the UV-Vis spectrometer. The glass substrate gave a near 100% transmittance without any observable absorption peak, and this was expected, since the calibration was performed with the glass substrate.

![UV-Vis spectra for the Pd single layer thin films.](image)

Fig. 6.4. UV-Vis spectra for the Pd single layer thin films.
Fig. 6.5 Plot of $\ln(T)$ against the Pd film thickness $x$ for the single layer films ranging from 2 nm to 35 nm in thickness. $x = 0$ nm for the case when only the glass substrate is present.

The transmittance results for the single layer films obtained from Fig. 6.4 were converted to $\ln(T)$ and plotted against the thickness of the film, as in Fig. 6.5, which yielded a linear plot with a negative gradient and a $y$-intercept almost equal to zero, which is in excellent agreement with Eq. 6.3. The gradient of the plot would readily give us the absorption coefficient, $\alpha$, of the Pd. The linear least squares fitting gave an experimental value of $\alpha$ for the Pd single layer film series to be 0.0894 nm$^{-1}$, which is within 2% of the value obtained for Pd: 0.0885 nm$^{-1}$ at 530 nm wavelength [22], calculated based on Eq. 6.2. The 2% close proximity between the experimental value of the absorption coefficient and the established value, together with the square of the correlation coefficient ($R^2$) value of 0.9984, provides an indication of the accuracy of the Pd film thickness measurements in this work.
6.3.1.2 Multi-stacked Pd-C$_{60}$-Pd thin film structures

Fig. 6.6(a) shows the UV-Vis spectra for the multi-stacked Pd(10nm)-C$_{60}$-Pd(10nm) thin film structures with C$_{60}$ layer thickness of 5 nm, 10 nm, and 20 nm. As with the spectra of the single layer films, the spectrometer was calibrated with the glass substrate, and a run with the glass substrate was again performed to ensure proper calibration, which gave the expected transmittance value of 100% [Fig. 6.6(a)].

The spectrum for a 20 nm pale yellowish, tinted transparent C$_{60}$ film deposited on glass substrate has been included in the figure for spectral signature comparison. The UV-Vis spectra of the multi-stacked film structures with sandwiched C$_{60}$ layer thicknesses of 20, 10, and 5 nm showed the same absorption peak around the wavelength of 345 nm wavelength as the pure C$_{60}$ film on glass substrate [Fig. 6.6(a)]. Fig. 6.6(b) shows a close-up view of a small but observable absorption peak in the spectra of the Pd-C$_{60}$(5nm)-Pd film structures around the 345 nm wavelength. These UV-Vis spectroscopy measurements provided confirmation that the material of the sandwiched layer between the two 10 nm Pd films in the stacked structures was C$_{60}$.

The UV-Vis results also suggest that the C$_{60}$ film could be suitable for optical applications of thin films where a high transmission from 550 nm (green) to 800 nm (near infrared) is desirable, as evidenced by the C$_{60}$ spectrum in Fig. 6.6(a).

The transmittance, $T$, for the multi-stacked film structures was lower, as expected, than that of the single layer 10 nm Pd film, which has a $T$ value of 46.7% at the wavelength of 550 nm. From Eq. 6.1, if we double the film thickness to $2x$, then the resultant transmittance value will be $T^2$. Given that the multi-stacked film structures effectively consist of a pair of 10 nm single Pd films, the measured $T$ value of 23.4% at 550 nm for the multi-stacked film structures was not too far off from the estimated value of
21.8% \((100 \times 0.467^2)\), neglecting the absorption of the \(\text{C}_6\text{O}\) layer and all other effects, such as multiple reflections in multilayer periodic thin films of varying refractive indices.

Note also that there are significant overlaps of spectra among the multi-stacked film structures in the wavelength range of 550 nm to 800 nm. The overlaps in the spectra (i.e. similar transmittance values at a given wavelength) tell us that the vacuum evaporated 10 nm Pd films in the stacked film structures were highly uniform in thickness, given that the measured transmittance of the stacked structures has an exponential dependence on the Pd film thickness, \(x\), as in Eq. 6.1. Based on the experimental value of the absorption coefficient, \(\alpha\), of 0.0894 nm\(^{-1}\) obtained for the evaporated Pd films from UV-Vis spectroscopy, a reduction of 1 nm in the designed film thickness of 10 nm will result in an increase of 3.83% in the \(T\)% value. As for the difference in transmittance, \(T\)% values among the multi-stacked Pd-C\(_6\text{O}\)-Pd film structures varied by less than 1% in the wavelength window of 550 to 800 nm, and this implied that the variation in the total thickness of the Pd films among the multi-stacked Pd-C\(_6\text{O}\)-Pd film structures was less than 1 nm.
Fig. 6.6 (a) UV-Vis spectroscopy results for the multi-stacked film structures Pd-C$_{60}$-Pd. (b) Close-up view around the 345 nm wavelength region highlighting the small but detectable C$_{60}$ absorption peak for the Pd-C$_{60}(5\text{nm})$-Pd sample.
6.3.2 Crystal structures and surface morphology

Fig. 6.7 shows the XRD results for the single layer Pd films 10, 17, 23, and 35 nm in thickness in comparison to a bulk 2 mm Pd sheet. The range of 2θ angles from 35 to 55 covers the two primary XRD peaks of bulk Pd, i.e. the [111] peak at 40.18° and the [200] peak at 46.74°, which are matched well against ICDD database file number 87-639 for Pd. Peaks around 2θ = 37.7° and 44.0° have originated from the sample holder and are marked with “SH”. The 35 nm film exhibited a much stronger preferred orientation along the [111] direction than the bulk Pd sheet. There were no XRD peaks observed for the 10 nm Pd film, which could imply either that the diffracted x-ray intensity from the sample was below the detection limit of the detector or that the evaporated film was amorphous at such a thickness.
Fig. 6.8 shows the AFM image for the 10 nm Pd film in 3D. The rms surface roughness of the Pd film and the glass substrate was determined to be 2.419 nm, and 0.893 nm, respectively. The “micro-scratch” was likely to have originated from the glass substrate and it influenced the grain growth of the film during deposition.

![AFM image of the 10 nm Pd ultrathin film on glass substrate in 3D.](image)

6.3.3 Contrast and switching speed measurements

6.3.3.1 Pd single layer thin films

Fig. 6.9(a) shows the change in the contrast for the series of single Pd thin films with thicknesses of 5, 10, 17, 23, and 35 nm as a function of time after 0.3 atm of H₂ was injected into the evacuated optical cell. We could see that the Weber contrast increased with the film thickness. The contrast of the films was normalized, as shown in Fig. 6.9(b), and plotted with the data points shown for ease of comparison of switching speed among the Pd single layer films. The time interval between the data points was 0.25 s. From Fig. 6.9(a) and (b), it is clear that thicker films have a higher optical
contrast, but longer response time, which is consistent with expectation. The 5 nm film has a response time of 0.5 s, while it took 50 s for the 35 nm film to achieve the same fractional level of completion. On the other hand, the 35 nm Pd film has a Weber contrast of 0.69 when fully hydrogenated at 0.3 atm H$_2$, while the 5 nm film has a switching contrast of only 0.042, which is 6.1% of that of the 35 nm film. The 10 nm Pd film has a Weber contrast of 0.81 and a response time of 1.4 s. Fig. 6.9(c) shows the response-recovery times for the 2 nm Pd single layer film at room temperature. Because the film was only 2 nm thick, it took only 0.25 to 0.5 s to reach 80% completion, which was close to the time resolution limit of the optical detection system in the experimental setup. The 2 nm Pd film has a measured Weber contrast of only 0.01, which was about 10 times less than that of the 10 nm Pd film. Fig. 6.9(d) summarizes the Weber contrast and the response times (80% completion) for the Pd single layer film series from 2 nm to 35 nm.

Fig. 6.10 shows the switching speed during the recovery phase for the Pd single layer films 5 to 35 nm in thickness. The recovery time ranged from 4 s for the 5 nm film to 47 s for the 35 nm film. The Weber contrast during the recovery phase is not shown, as the Pd films generally absorbed and released hydrogen reversibly, including the 2 nm Pd film [Fig. 6.9(c)].
Fig. 6.9 (a) The Weber contrast for the single Pd films 5, 10, 17, 23, and 35 nm in thickness as a function of time when 0.3 atm H$_2$ was injected into the optical cell during the response phase. (b) Normalization of the switching contrast to enable ease of comparison of switching speed among the films of various thicknesses. (c) The response-recovery temporal profile for the 2 nm single layer Pd film. (d) The variation in the Weber contrast and the response time as a function of film thickness.
6.3.3.2 Multi-stacked Pd(10nm)-C$_{60}$-Pd(10nm) film structures

Fig. 6.11(a) shows the switching contrast for the stacked Pd(10nm)-C$_{60}$-Pd(10nm) film structures with different thicknesses of C$_{60}$. The 10 nm and 17 nm single layer Pd films, as well as the dual-10 nm samples, are included for comparison. The switching contrast values for the stacked films were reasonably close to each other, and these switching contrasts were about 0.19, which is approximately twice the measured contrast of 0.082 for the single 10 nm Pd film. The 20 nm C$_{60}$ film deposited on glass was included in the optical cell test to verify that the sandwiched C$_{60}$ layers in the multi-stacked film structures made a negligible Weber contrast contribution as the stacked structures were hydrogenated, and the results are plotted in grey color in Fig. 6.11(a) with circular data markers visible and with the annotation “C$_{60}$''. Note also that the stacked films have similar contrast to the physically cascaded dual-10 nm film, except that the latter has a switching contrast slightly lower than that of the multi-stacked film structures. This is probably due to the fact that the incident 530 nm green light experienced greater optical
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reflection as it propagated through the dual-10 nm film than it did in the multi-stacked film structures, due to the differences in the refractive index environment in these two structures, with the refractive index of hydrogen gas being close to 1.0, while the refractive index of the C\(_{60}\) layer is about 2.2. The refractive index of Pd is 1.6 at 530 nm wavelength.

The normalized plot in Fig. 6.11(b) shows a comparison of the switching kinetics of the Pd-C\(_{60}\)-Pd film structures during the response phase. The Pd-C\(_{60}\)(10nm)-Pd and the Pd-C\(_{60}\)(20nm)-Pd had a response time comparable with that of the 10 nm single layer Pd film and the dual-10 nm Pd film, and they all achieved 80% completion between 1.1 and 1.8 s, with the stacked films slightly lagging behind the single layer films. They were all faster than the 17 nm single Pd film (3.5 s) of comparable Weber contrast (0.204). An exception is the Pd-C\(_{60}\)(5nm)-Pd, as it was found to have an 80% completion time of 6.4 s, which was slower than that of the 17 nm films.

Fig. 6.11(c) shows the recovery time for the same samples of film, and again, the Pd-C\(_{60}\)(10nm)-Pd and the Pd-C\(_{60}\)(20nm)-Pd had similar recovery time to the 10 nm single layer Pd film, with recovery time of about 10.6 s (20% completion). The 17 nm film had a recovery time of 28.75 s, which was about 2.7 times slower than for the Pd-C\(_{60}\)-Pd film structures. The Pd-C\(_{60}\)(5nm)-Pd again recovered much more slowly than the other two stacked film structures, with a recovery time of 27 s, which was comparable to that of the 17 nm single Pd film. Apart from the Pd-C\(_{60}\)(5nm)-Pd, the collective results presented in Figure 6.11(a) to (c) indicate that the Pd-C\(_{60}\)-Pd multi-stacked films had a switching contrast similar to that of a thicker 17 nm single layer Pd film, yet they had response and recovery times comparable to those of the thinner 10 nm single layer Pd film. In other words, the switching contrast of a 10 nm Pd ultrathin film can be greatly enhanced with the application of such a multi-stacked structure while preserving much
of the crisp response and recovery speeds of the ultrathin film. The 17 nm single layer Pd film had a longer response-recovery switching time than the 10 nm single layer Pd film, despite having about twice the switching contrast.

A plausible explanation for the slow switching speeds of the Pd-C$_{60}$(5nm)-Pd relative to the other two multi-stacked film structures might be that there was a significant quantum interaction associated with the 5 nm C$_{60}$, given its low nanoscale dimension, such that it strongly influenced the hydrogen diffusion behavior during the hydrogen de/absorption process into and out of the Pd stacked structure. More experimental tests and first principles studies will be needed to ascertain the cause of such an effect.

(a)
Fig. 6.11 (a) The switching contrast of the multi-stacked Pd-C$_{60}$-Pd film structures was roughly double that of the 10 nm single layer Pd film. The 20 nm C$_{60}$ film evaporated on the glass substrate is included in the plot. (b) and (c) show that both the Pd-C$_{60}$(10nm)-Pd and the Pd-C$_{60}$(20nm)-Pd were able to optically switch in a similar time to the single 10 nm Pd film during the response (b) and recovery (c) phases, while the Pd-C$_{60}$(5nm)-Pd film had a much reduced switching speed.
6.3.4 Hydrogen diffusion pathway

Fig. 6.12 gives a comparison of the response phase switching time for samples with various seal configurations: Asii, EdgS, SurfS, and ComS, and with C₆₀ sandwich layer thicknesses of 10 nm, 20 nm, and 60 nm. The numbers in the plot legend in the figure denote the thickness of the C₆₀ layer of the multi-stacked film structures. The EdgS configuration basically switched as fast as the Asii for the PdC₆₀(10nm)-Pd film structure, if we take into account the estimated experimental uncertainty in hydrogen diffusion time of ± 0.15 s due to factors such as the intrinsic fluctuation in the local hydrogen concentration in the vicinity of the film inside the optical cell. On the other hand, the 10 nm SurfS only reached 80% completion in 386 s (6.4 minutes), while the 10 nm ComS reached 36% completion in the same time period. These results, if taken together, strongly suggest that the primary channel of hydrogen diffusion in the PdC₆₀(10nm)-Pd film structure is likely to be from the surface of the top Pd layer, and there was little or no contribution from the edge diffusion pathway. The reason as to why there was still hydrogenation of the Pd films taking place in the 10 nm ComS sample was probably because the adhesive tape was not entirely resistant to hydrogen diffusion, given the small size of molecular hydrogen.

We repeated the same test procedure on the Pd-C₆₀(20nm)-Pd and the Pd-C₆₀(60nm)-Pd to see if there is any edge diffusion contribution for stacked structures with a thicker layer of C₆₀. However, test results consistently showed that the EdgS samples had similar switching time to the Asii samples for both the Pd-C₆₀(20nm)-Pd and the Pd-C₆₀(60nm)-Pd multi-stacked structures. Furthermore, the switching performances for the SurfS and ComS configurations of these films were similar to those of the Pd-C₆₀(10nm)-Pd. We could also see that the optical switching times of these structures become progressively longer as the C₆₀ layer becomes thicker from 10 nm to 60 nm,
which was as expected. The 80% completion times for the 10 nm Asii, 20 nm Asii, and 60 nm Asii samples were 1.45 s, 1.9 s, and 2.3 s, respectively.

This work presents the proof of principle by using only a pair of Pd films, however, the concept of switching contrast enhancement could well be extended to a superlattice structure based on 2 to 5 nm Pd films, as well as other suitable metal-hydride ultrathin films. Materials such as polymers could also be explored as suitable interlayers between the metallic films, and it may be useful to study the hydrogen diffusion in ultra-low nanometer C_{60} film, e.g., 1 to 5 nm, in greater detail. Furthermore, the concept of the multi-stacked or superlattice configuration could well have benefits for hydrogen storage media. Promising hydrides in the form of single layer ultrathin films often have improved kinetics and thermodynamics (such as a lowered temperature of hydrogen desorption), which is essential for mobile applications. The concept of the multi-stacked or superlattice configuration demonstrated herein could be employed, with such ultrathin films closely stacked on the nanometer scale, so that a higher hydrogen storage capacity could be achieved in term of volumetric density, while retaining much of the unique hydrogen storage properties of ultrathin film.
6.4 Conclusions

We have proposed and demonstrated a multi-stacked structure intended for ultrathin film switchable mirror applications with the advantage of enhanced switching contrast, while simultaneously preserving much of the fast switching speed commonly associated with ultrathin films. We have also fabricated single layer Pd films 2 to 35 nm in thickness. The 5 and 10 nm ultrathin film had a response time (80% completion) of 0.5 and 1.3 s, respectively. The “proof-of-principle” Pd(10nm)-C_{60}(10nm)-Pd(10nm) structure had a response time of 1.45 s. The demonstrated concept of the multi-stacked structure could therefore be used in important applications of dynamic switchable mirrors such as smart windows and hydrogen gas sensors, which require sub-second response times and high contrast. UV-Vis spectroscopy transmittance results have validated the Pd single layer thin film thickness measurements ranging from 2 to 35 nm.
Hydrogen diffusion pathway tests suggested that surface diffusion via the Pd top layer is the primary diffusion channel, based on the observation that the “edge-sealed” Pd-C$_{60}$ Pd samples had similar response time to the “As-it-is” samples. The diffusion contribution via the edges of the stacked structure was negligible by comparison for the sandwiched C$_{60}$ layers with thickness ranging from 10 up to 60 nm. A superlattice structure will be fabricated in the future based on 2 to 5 nm Pd thin films, and other materials such as polymers may be explored as suitable interlayers between the metallic films. The concept of a multi-stacked/ superlattice structure could also be applied to hydrogen storage materials in the form of ultrathin film to increase the effective volumetric hydrogen storage capacity for mobile applications.

6.5 References


CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The main objectives of this research project have been achieved. Four sets of different but related experiments have been successfully carried out that covered important aspects of the hydrogen economy, namely hydrogen storage and novel characterization techniques for nano-hydride research, as well as switchable mirrors for applications such as hydrogen gas sensing and smart window technology for energy conservation.

7.1.1 Mg nanopowder catalyzed by Ti and Ni/Ti

Target application: hydrogen storage

In this research, magnesium was ball-milled with nickel (Ni) and titanium (Ti) in different amounts and with different mixing ratios between the Ni and Ti in 7 atm hydrogen pressure. The Ti and Ni/Ti additives were found to successfully reduce the activation energy (and hence the desorption time) of MgH$_2$ with varying degree of effectiveness, and the activation energy dropped from 250 kJ·mol$^{-1}$ for pure as-milled MgH$_2$ down to 81 kJ·mol$^{-1}$ for the sample with Ni/Ti (Ni:Ti = 4:1, 26.7 at.% Ni). The hydrogen release time (80% completion) consistently dropped with activation energy to a minimum of 30 s.
In terms of thermodynamics, however, the maximum improvement in the desorption temperature was only 22 °C, and that was achieved with the MgH$_2$ sample with the Ni/Ti (4:1 ratio) additive.

The sample with Ni/Ti (4:1 ratio) gave the overall best hydrogen desorption performance, and this may be attributed to the synergetic catalytic effect between Ni and Ti. Work based on first-principles calculations will be performed to study the Ni–Ti catalysis system in view of its importance and the seemingly intriguing synergetic effect. Such a synergetic mechanism may well be applicable to other hydrogen storage material systems.

### 7.1.2 Reflective optical detection for Mg nanowires and nanostructures

**Target application: Novel characterization technique for nano-hydride research**

We have demonstrated that the desorption temperature and kinetics of magnesium hydride in powder form can be obtained from a relatively straightforward measurement of the change in light intensity reflected off the sample in the visible range. This optical technique can potentially be used to measure the de/absorption temperature and kinetics of magnesium nanostructures, which are often fabricated via the physical vapor deposition (PVD) method inside an optically transparent quartz tube. It can also be applied to other hydrogen storage materials in powder form that exhibit change in optical absorption during the de/hydrogenation process.

Future work will involve building an optical cell that can withstand hydrogen pressure up to approximately 20 atm and replacing the basic soldering iron with a proper temperature-controlled microheater. We hope that the new setup will enable us to investigate the ability of the optical system to measure the kinetics of ab/desorption of
suitable hydrides at fixed temperature by varying the pressure of the cell and to generate pressure-composition-isotherm (PCI) curves to obtain a more accurate desorption temperature.

7.1.3 Mg thin films

Target application(s): switchable mirrors / hydrogen storage

We fabricated an 11 nm magnesium ultrathin film capped with 2 nm Pd. Optical transmission characterization of the film showed that it was capable of hydrogen de/absorption with 80% completion in about 3 minutes in air at 25°C. The hydrogen pressure during the absorption test was 0.25 atm. Experimental results of this research also support the hypothesis put forward by other research groups that the catalytic Pd acts as the gateway for the passage of hydrogen, even though parts of the surface of the Mg film may be oxidized, making the Mg film underneath inaccessible to hydrogen diffusion.

Raman measurements showed shifting and broadening of the $E_g$ mode associated with strong hydrogen-hydrogen interaction within the hydride. Both the phonon calculations performed in CASTEP and the Raman measurements of the bulk MgH$_2$ at room temperature and pressure using the 632 nm excitation line are shown to be in good agreement with each other in terms of the vibrational Raman frequencies and the relative intensities, including the frequency of the main $E_g$ vibrational mode centered around 940 cm$^{-1}$. 
7.1.4 Pd-C$_{60}$-Pd film structures

Target application(s): switchable mirrors / hydrogen storage

The idea of a multi-stacked structure has been proposed and successfully demonstrated experimentally. The film structures consist of layers of hydrogen storage material interspaced with hydrogen-permeable layers. The proposed thin film architecture was designed to enhance the contrast of hydride-based ultrathin film with little or no retardation of the intrinsic high switching speed of the ultrathin film.

The “proof-of-principle” film structure was based on Pd(10nm)-C$_{60}$(10nm)-Pd(10nm), and it had a response time of 1.45 s. The demonstrated concept of such a multi-stacked structure could be used in important applications of dynamic switchable mirrors such as smart windows and hydrogen gas sensors, which require sub-second response times and high contrast.

A superlattice structure will be fabricated in the future based on 2 to 5 nm Pd thin films, and other materials such as polymers may be explored as the suitable interlayers between the metallic films. The concept of the multi-stacked/ superlattice structure could also be applied to hydrogen storage materials in the form of ultrathin film to increase the effective volumetric hydrogen storage capacity for mobile applications. Other suitable experimental techniques could also be used to verify the hydrogen diffusion pathway.
7.2 Future work

One of the main challenges in hydrogen storage is to lower the desorption temperature of various promising hydrides such as MgH₂ and LiBH₄. Therefore, three research directions are proposed for future work as follows.

7.2.1 Nano-stage setup for the investigation of MgH₂ properties on the sub-nanometer scale.

In Chapters 5 and 6, the optical properties of hydride were successfully been exploited to characterize hydride thin films. In this future work, the possibility of creating magnesium nanowires whose width is reduced to below 1 nm will be explored. The aim is to study the electrical properties of such a system before and after hydrogenation. Correlation with the chemical thermodynamics (and hence, \( T_{\text{des}} \)) will also be studied.

Fig. 7.1(a) shows a proposed nano-stage setup that may help to achieve this research objective. The preliminary plan is to pattern a pair of planar Mg electrodes linked by a Mg bridge nanowire using electron-beam lithography and focused ion beam (FIB) milling. The planar Mg electrodes will be deposited on top of piezo actuators, and the entire system will be built on a suitable substrate.

We hope to be able to achieve an initial Mg nanowire diameter of 30 to 50 nm. The piezo actuators will then be energized to stretch the nanowire so that its diameter will be further reduced to less than 1 nm. Hydrogen can be introduced at room temperature at any time to transform the nanowire into hydride whenever needed.
The details on the electrical properties of such a system is the subject of the research, however, it is expected that when the diameter of the Mg nanowire is reduced so that it becomes comparable to the de Broglie wavelength of the conduction electrons, the absence of scattering will result in ballistic electron transport and the conductance will become quantized [1–4].

The conductance is given by the Landauer formula

$$G = N \frac{2e^2}{h}$$ (7.1)

where $2e^2/h \approx 13 \text{ k}\Omega^{-1}$ is the conductance quantum per electron spin, and $N$ is the number of conducting channels.

An example of a staircase-like quantized conductance, $G$, during closure of a contact between two macroscopic gold wires under ambient conditions is shown in Fig. 7.1(b), and it is evident that conductance plateaux occurs at multiples of $2e^2/h$. 
Fig. 7.1 (a) The proposed nano-stage setup. The pair of the piezo actuators will stretch and reduce the diameter of the Mg nanowire down to atomic dimensions. (b) An example of quantized conductance showing the conductance plateaux at multiples of $2e^2/h$ [image taken from Ref. 5].
7.2.2 Resonant photodesorption of hydrogen

In 2006, a research group at the University of Minnesota reported the desorption of hydrogen from a Si(111) surface by resonant excitation of the Si-H vibrational stretching mode [6]. The incident light source was a free-electron laser (FEL) capable of delivering a maximum of 100 mJ per macropulse at a repetition rate of 30 Hz [6]. The experiment was carried out in an ultrahigh-vacuum system at a base pressure of approximately $3 \times 10^{-10}$ Torr. The sample was exposed to the FEL illumination at room temperature, and the desorbed hydrogen was pumped away by an ion pump.

The group found that the hydrogen desorption yield peaked at a wavelength of 4.8 µm (0.26 eV), as shown in Fig. 7.2, where the energy of the incident radiation corresponds to the energy of the vibrational stretch mode of Si-H bond on the terrace sites of the Si(111) surface [6]. Hydrogen desorption was not observed when the incident wavelength was far from the resonant wavelength of 4.8 µm, and this observation provided solid evidence that direct laser heating was not the main desorption mechanism.

The researchers also performed other tests in an attempt to rule out hydrogen desorption due to laser heating, including a study of the polarization dependence of the hydrogen desorption yield. They found that the desorption yield changed with the polarization angle, $\theta$, as a function of $\cos^4 \theta$, as shown in Fig. 7.3, and the group concluded on the basis of this that the observed desorption could not have resulted from a thermal process caused by direct laser heating, but rather from the direct interaction between the incident field and the Si-H bonds [6]. The $\cos^4 \theta$ dependence also implies a quadratic relationship between the desorption yield and the fluence of the FEL, as shown in Fig.
7.4, and this quadratic dependence is a significant departure from the approximately
ninth-order dependence reported for the case of multiple vibrational excitation of
hydrogen on an Si(100) surface by scanning tunneling microscope (STM) [7]. It has
been pointed that the precise underlying desorption mechanism is still to be identified.

The comprehensive and careful research work performed by this group has inspired us
to make an attempt to apply the same principle of “hydrogen desorption via vibrational
stretching mode excitation” to hydrogen storage materials such as MgH$_2$ and LiBH$_4$, to
see if we too can observe hydrogen desorption from these samples at room temperature
under the right conditions, such as with the correct incident wavelength and polarization
angle.

Given that the desorption yield is likely to be affected by the polarization angle, we
expect that samples prepared in the form of thin films will have significantly higher
desorption yields than samples in powdery form. Lithium borohydride, LiBH$_4$
mentioned in Chapter 2 (literature review), has a well-known infrared-active B-H
stretching mode around 2306 cm$^{-1}$ [8], which would correspond to a wavelength of 4.33
$\mu$m. Therefore, if the principle of resonant photodesorption were to hold equally true for
LiBH$_4$, then we would expect to see the dissociation of the B-H bonds at room
temperature when an infrared light of wavelength 4.33 $\mu$m is used to irradiate the LiBH$_4$
thin film at the correct polarization angle. The intensity of the incident infrared radiation
will have to be determined as part of the future research efforts.
Chapter 7

Fig. 7.2 Dependence of the hydrogen desorption yield on the incident wavelength [6].

Fig. 7.3 Polarization dependence of the desorption yield (squares). The FEL fluence was kept at 0.8 Jcm⁻² per macropulse for all polarizations [6].

Fig. 7.4 Log-log plot of the desorbed hydrogen as a function of the FEL fluence. The polarization was 0° for all fluences, and the wavelength was tuned to 4.8 µm [6].
7.2.3 Surface plasmon nanophotonics

Surface plasmons are collective charge oscillations that occur at the interface between conductors and dielectrics [9]. They can take various forms, ranging from freely propagating electron density waves along metal surfaces to localized electron oscillations on metal nanoparticles [9]. The phenomenon of surface plasmons could lead to applications such as light guiding and manipulation on the nanoscale, ultrafast all-optical processors, biodetection at the single molecule level, and high resolution optical imaging below the diffraction limit [9–11]. In 2000, Prof. Harry Atwater and his research group at the California Institute of Technology named this emerging discipline “plasmonics” [11]. My research collaborator and I have recently applied surface plasmon resonance (SPR) to organic solar cells to improve the power conversion efficiency with great success [12].

It is my sincere hope that the focus given to both the mode resonance and the SPR proposed in this chapter could usher in an entirely new research direction in an effort to dramatically improve the energy efficiency of hydrogen desorption of promising hydrides such as MgH$_2$ and LiBH$_4$, thereby making them a truly practical hydrogen storage material for medium-weight vehicles and thus realize the hydrogen economy, which until now, remains very much an endearing dream.
7.3 References


5 http://physicsworld.com


List of Publications


Scanning electron microscope (SEM) images showing examples of magnesium-based structures fabricated in our laboratory using the physical vapor deposition method.
The noblest pleasure is the joy of understanding.

- Leonardo DaVinci

Somewhere, something incredible is waiting to be known.

- Carl Sagan

Our Song of Love can flood the Earth like a rising tide: releasing old paradigms of Fear and Duality, and allowing ourselves to Ascend to the higher vibrational levels of Unconditional Love and Oneness with All That Is.

- The humanity healing network