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Abstract

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Keywords

100, surfaces, thioacetyl, protected, alkynethiol, preparation, monolayers, thiol, terminated, silicon

Disciplines

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Preparation of thiol-terminated monolayers on silicon(100) surfaces using thioacetyl-protected alkynethiol

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Abstract—The attachment of acetyl-protected alkynethiol groups onto silicon(100) surfaces was achieved using a hydrosilylation methodology. Subsequent deprotection of the thiols using either hydrochloric acid or ammonia solution was investigated using X-ray photoelectron spectroscopy (XPS), and compared with similar reaction in solution. It was found that ammonia solution was more efficient than hydrochloric acid for the deprotection step. However, the deprotection was much less efficient on the surface than in solution.

Keywords— silicon; hydrosilylation; thiol; protection group; self-assembled monolayer

I. INTRODUCTION

Surfaces presenting thiol functional groups have applications in molecular electronics,[1,2] biochemistry,[3,4] and gold nanoparticle attachment.[5] For many of these applications, there is a need to present the functional groups on the surface in an ordered and controllable way. Self-assembly monolayers (SAMs) are an excellent platform for this purpose.

In 1995, Linford *et al.* showed that 1-alkenes and 1-alkynes could react with silicon(111) surfaces by a thermal hydrosilylation reaction to form stable and well-ordered SAMs where the bond at the silicon surfaces was *via* a Si-C linkage.[6] This kind of SAM is more robust and chemically stable than either traditional alkanethiol or silane SAMs.[6]

Sieval *et al.* showed that the hydrosilylation reaction can be performed on silicon(100) surfaces as well to produce good quality SAMs.[7] However, if the alkene or alkyne contains functional groups that could react with the hydrogen-terminated silicon surface, inhomogeneous monolayers would be formed, and the desired functional group would be lost.[7]

Since thiols can react with the hydrogen-terminated silicon surfaces, the thiol group needed to be protected.[1,5] The use of the trifluoroacetyl protection group for this purpose has been reported previously. [1,5] The advantages of this protecting group are that it is very easy to remove and does not affect the packing of the SAM by steric hindrance [1]. However, the trifluoroacetyl-protected alkynes and alkenes are not commercially available. Also, they are prone to hydrolysis.

To strike a balance between stability of the protected precursor and ease of deprotection on surface, the potential of the acetyl protection group as such a candidate would be explored in this paper.

II. EXPERIMENTAL SECTION

Materials

Silicon wafers (Virginia Semiconductor, Inc.) were double side polished, boron doped, 0.50 mm thick, resistivity 0.001-0.005 Ω cm. Sulfuric acid, hydrofluoric acid and hydrogen peroxide (Riedel de Hahn, Sydney, Australia) for the hydrosilylation reaction were semiconductor grade. Sodium hydroxide (analytical reagent grade), magnesium sulfate, hydrochloric acid (32%) and ammonia (28%) were obtained from Ajax Finechem, Sydney, Australia. Organic solvents were distilled before use. Thioacetate **1** was synthesised using the procedure reported previously.[8] Thin-layer chromatography (TLC) was performed on Merck silica gel 60F234 aluminium sheets. All other chemicals, unless stated otherwise, were used as received without further purification.

Deprotection of the thioacetate **1** in solution using acid (figure 1)

The details of deprotection of the thioacetate **1** using hydrochloric acid were reported earlier.[1, 9] In brief, the thioacetate **1** was dissolved in deoxygenated 95% ethanol : 32% HCl (75:1, v/v) and heated at reflux under nitrogen atmosphere. The extent of deprotection was monitored using TLC, until no starting materials could be detected.

Deprotection of the thioacetate **1** in solution using base (figure 1)

To a 3-neck flask under nitrogen atmosphere was loaded the thioacetate **1** (*ca.* 40 mg). Either sodium hydroxide (2 M deoxygenated aqueous solution) or ammonia (15 M, diluted

with 5x (v/v) deoxygenated 95% ethanol) was added. The reaction mixture was then stirred overnight under nitrogen at room temperature. After that, the reaction mixture was acidified to around pH 6 with hydrochloric acid (10 M), monitored by pH paper. The mixture was then diluted with water (*ca.* 5 mL) and extracted with ether (3 x 10 mL). The organic portion was dried (MgSO_4), and evaporated *in vacuo* to obtain the crude thiol **2**. The reaction yield was estimated using ^1H NMR (300 MHz, CDCl_3), by comparing the intensity of the peak around δ 2.84 (t, 2H, $J = 7.1$ Hz, CH_2SAc in **1**) and the peak at around δ 2.48 (q, 2H, $J = 7.5$ Hz, CH_2SH in **2**).

Preparation of surfaces

The preparation of surface **S2** (figure 2) was reported previously.[8,9] Surface **S2** was immersed in distilled (under reduced pressure), degassed (at least 5 freeze-pump-thaw cycles) thioacetate **1** in a Schlenk flask under argon at 120°C overnight to afford surface **S3**. Surfaces **S3** were then placed in either 15 M ammonia solution or 10 M hydrochloric acid to afford surface **S4**.

XPS measurements and analysis

XPS of the surfaces were acquired using an ESCALAB 220iXL spectrometer with a monochromatic Al $K\alpha$ source, hemispherical analyzer and multichannel detector. Binding energies were corrected with reference to Si 2p $_{1/2}$ signal (99.9 eV). Survey scans (0-1100 eV) were carried out with 1.0 eV step size, 100 ms dwell time, and pass energy 100 eV. High-resolution scans (Si 2p, S 2s, C 1s) were carried out with 0.1 eV step size, 100 ms dwell time, and pass energy 20 eV.

The XP spectra were analysed using the curve-fitting program XPSPEAK 4.1. The high-resolution scans were first background-subtracted using the Shirley method, then deconvoluted and fitted with peaks with mixed Gaussian-Lorentzian functions. The error of peak-fitting in each high-resolution scan region was represented by the χ^2 value. These χ^2 values were less than 1, indicating accurate fits. Atomic compositions of the surfaces were calculated using the peak area, number of scans, and atomic sensitivity of the elements.[9]

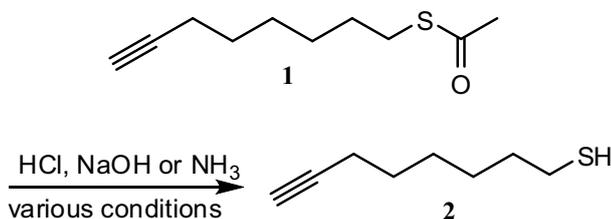


Fig. 1: deprotection of the thioacetate **4** to afford thiol **5**

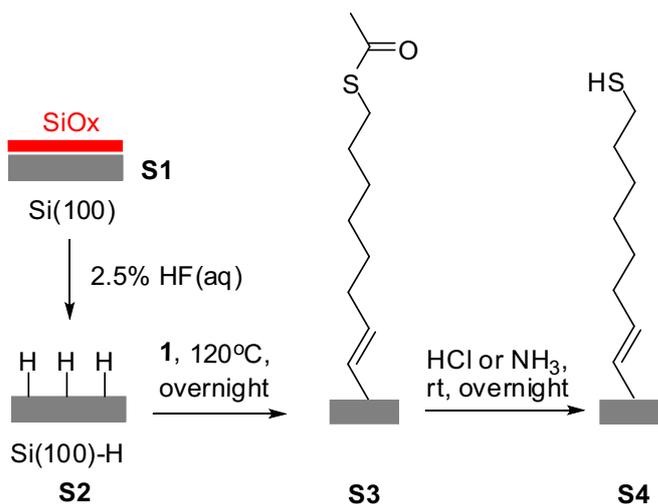


Fig. 2: Attachment of the protected thiol. **1** and subsequent reactions on Si(100) surfaces.

III. RESULTS AND DISCUSSION

Deprotection of thioacetate **1** in solution

The deprotection strategy needed to be established in bulk solution before applying to deprotection on surfaces. Several methods were attempted to remove the acetyl protecting group to form the thiol **2** (figure 1). Deprotection using hydrochloric acid (*ca.* 0.1 M ethanoic solution) were reported previously by Ciampi *et al.*, reacting at 60°C for 5 h and achieved 63% yield.[10] However, to achieve complete deprotection, the reaction required 48 h.

Subsequently, a basic deprotection procedure was explored. Using sodium hydroxide, reacting at room temperature overnight achieved approximately 20% deprotection. Alternatively, using ammonia, reacting at room temperature overnight achieved >95% deprotection. The above results show that ammonia is the most effective of the three reagents investigated for this process.

Attachment of thioacetate **1** to Si(100) to give surface **S3**

Figure 3a shows the C 1s high resolution XP spectrum of surface **S3**. The spectrum can be deconvoluted into three peaks: (i) *ca.* 285 eV, due to carbon atoms bonded to either another carbon atom or a silicon atom [1]; (ii) *ca.* 286.5 eV, due to either carbon atoms bonded to a sulfur atom [1] or oxidized carbon contamination [11]; (iii) *ca.* 288.5 eV, due to carbonyl carbons bonded to a sulfur atom [1].

Figure 4 shows the S 2s high resolution XP spectrum of surface **S3**, with a single peak at *ca.* 228.5 eV. It is about 0.5 eV lower than the sulfur atom bonded to trifluoroacetyl protecting group [1,8]. This may due to a lower electron-withdrawing ability of the acetyl group, compared with the trifluoroacetyl group, bonded to the sulfur atom.

The presence of all three C 1s and the S 2s peaks showed the attachment of thioacetate **1** onto the surface was successful.

Deprotection of thioacetate moiety on surface **S3**

After showing that both hydrochloric acid and ammonia could achieve nearly complete deprotection in solution, both deprotection strategies were investigated for deprotection of surface bound molecules, surface **S3**. Figure 3b shows the XP spectra of surface **S4**, formed by immersing **S3** in hydrochloric acid (10 M aqueous solution) overnight, while figure 3c showed the XP spectra of another surface **S4**, formed by immersing **S3** in ammonia (15 M aqueous solution) overnight. Comparing to figure 3a, the signal corresponding to the carbonyl carbon (*ca.* 288.5 eV), did not decrease significantly after hydrochloric acid treatment, but did decrease significantly after ammonia treatment. In contrast, the S 2s peak intensity was almost unchanged after undergoing either deprotection treatment. Quantitative analysis showed that the ratio of the carbonyl carbon to sulfur (calculated using the area of the carbonyl carbon peak and the area of S 2s peak, adjusted by the relative atomic sensitivity of sulfur and carbon) was 0.99:1 in **S3**, 0.87:1 after hydrochloric acid treatment and 0.46:1 after ammonia treatment. Therefore, the extent of deprotection was about 13% using hydrochloric acid and about 54% using ammonia. Similar to the reaction in solution, ammonia is more effective than hydrochloric acid for removing the acetyl group. However, these results also showed that the rate of deprotection on surface is significantly lower than that in solution.

IV. CONCLUSION

The above results show that ammonia is more effective than hydrochloric acid for removing the acetyl protecting group. While complete deprotection of this group is relatively easy to achieve in solution, complete deprotection on surfaces is less efficient. This inefficiency becomes more noticeable when compared to the trifluoroacetyl group, where only 10 mins at room temperature in aqueous ammonia is required to achieve complete deprotection.[1,5] Therefore, to prepare thiol-terminated SAMs on silicon surface, if the synthetically straightforward acetyl derivative is used, a much longer deprotection time and a higher deprotection temperature are needed. Otherwise, the more synthetically challenging trifluoroacetyl derivative is required.

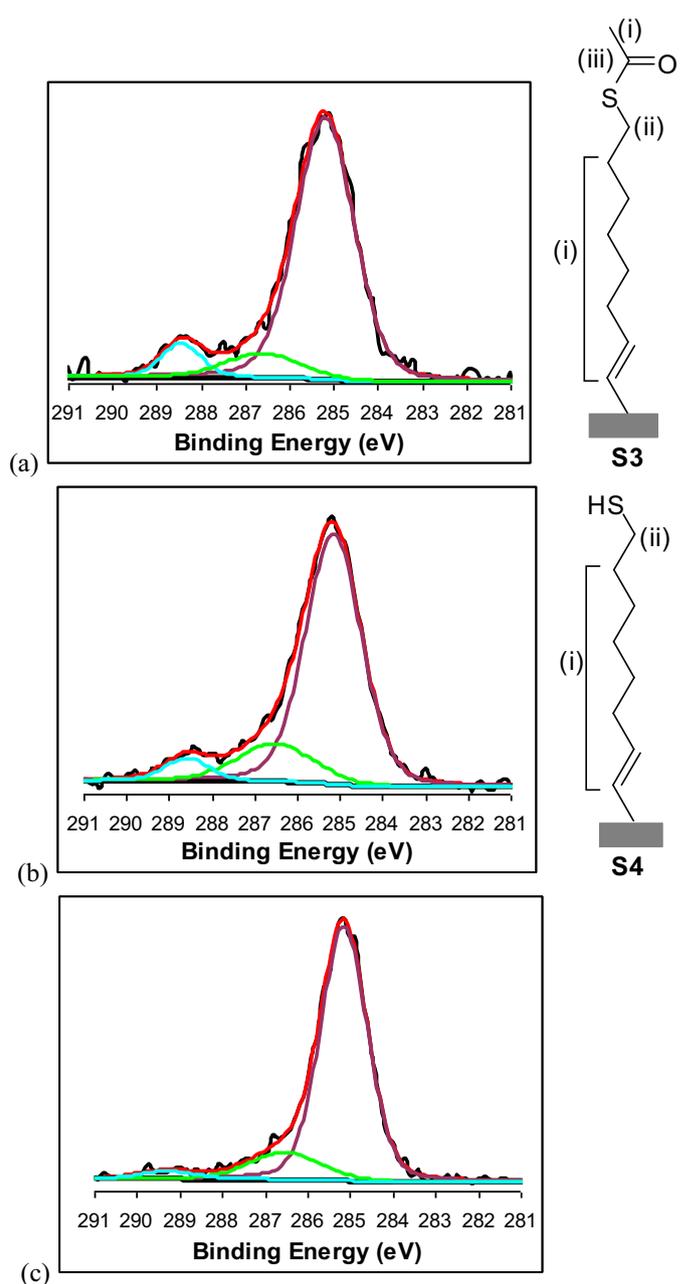


Fig. 3: C 1s high resolution XP spectra of surfaces: (a) **S3**; (b) **S4** by HCl route; (c) **S4** by NH_3 route. Peak assignment key: (i) purple; (ii) green; (iii) blue

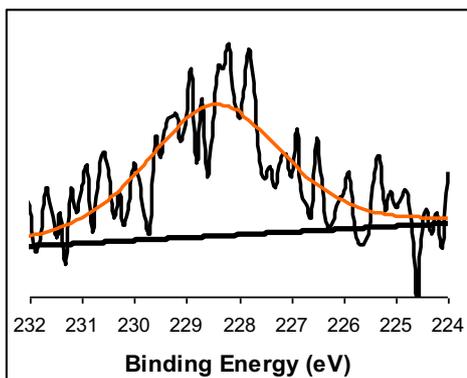


Fig. 4: S 2s high resolution XP spectrum of surface S3. The S 2s spectra of S4 (by HCl or NH₃ route) are very similar.

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