1-1-2010

Correlation of nanoindentation-induced deformation microstructures in diamondlike carbon coatings on silicon substrates with simulation studies

Ayesha J. Haq

University of Wollongong, ayesha@uow.edu.au

Paul G. Munroe

The University of New South Wales

Mark Hoffman

University of New South Wales

Phil J. Martin

CSIRO, Phil.Martin@csiro.au

Avi Bendavid

CSIRO, Avi.Bendavid@csiro.au

Follow this and additional works at: <https://ro.uow.edu.au/engpapers>

Part of the [Engineering Commons](#)

<https://ro.uow.edu.au/engpapers/3338>

Recommended Citation

Haq, Ayesha J.; Munroe, Paul G.; Hoffman, Mark; Martin, Phil J.; and Bendavid, Avi: Correlation of nanoindentation-induced deformation microstructures in diamondlike carbon coatings on silicon substrates with simulation studies 2010, 910-920.

<https://ro.uow.edu.au/engpapers/3338>

Correlation of nanoindentation-induced deformation microstructures in diamondlike carbon coatings on silicon substrates with simulation studies

Ayesha J. Haq,^{a)} Paul R. Munroe, and Mark Hoffman
*School of Materials Science and Engineering, University of New South Wales,
Sydney, NSW 2052 Australia*

Phil J. Martin and Avi Bendavid
CSIRO Materials Science and Engineering, Lindfield, NSW 2070 Australia

(Received 24 August 2009; accepted 9 November 2009)

The effect of the presence of diamondlike carbon coatings deposited on (100) Si substrates on the deformation mechanisms operating in the silicon substrate during contact loading have been investigated by both cross-sectional transmission electron microscopy and modeling of the stresses generated beneath the indenter tip. The observed subsurface microstructures were correlated to the Tresca shear stress and the hydrostatic stress generated in the silicon substrate beneath the indenter tip. The presence of the coating altered the stresses generated in the substrate, and changed the deformation mechanism from one of principally phase transformation in uncoated Si to predominantly dislocation motion in the silicon substrate for the diamondlike C–Si system. The magnitude and distribution of the shear and hydrostatic stresses in the substrate were found to depend on both the indentation load and the thickness of the coating. Furthermore, the observed width of deformation, parallel to the interface, which was found to increase with coating thickness, was correlated to the wider distribution of the Tresca shear stress in the substrate brought about by the presence of the coating.

I. INTRODUCTION

The deformation of Si under contact loading has been widely studied^{1–13} and it is generally accepted that in uncoated silicon phase transformation, rather than dislocation nucleation, is the dominant deformation mechanism.^{4–7,10–14} Page et al.⁴ and Callahan and Morris⁵ observed that densification, or phase transformation, was the first plastic response to indentation in Si. This led to the suggestion that densification or phase transformation occurs in Si before the critical shear stress for dislocation nucleation is reached.¹⁴ Later, Bradby et al.^{11,12} observed slip in indented Si, regardless of whether the applied load exceeded that required to induce a discontinuity or pop-in in the load–displacement curve. Furthermore, they also observed that phase transformation occurs before the observance of pop-ins, and suggested that a pop-in occurs due to the sudden extrusion of the highly plastic transformed material beneath the indenter tip. Subsequently, Lorenz et al.¹⁵ compared the ratio of maximum hydrostatic pressure and the maximum shear stress calculated from contact theory (which for Si is 2.8 at a Poisson's ratio, ν of 0.35) with the ratio of hydrostatic

pressure and the stress of homogenous dislocation nucleation in different materials. These authors concluded that since the ratio of the minimum hydrostatic stress required for phase transformation and the critical shear stress for homogeneous dislocation nucleation for Si is lower than 2.8, phase transformation is initiated before shear stress is reached and therefore the pop-in effect cannot be attributed to dislocation nucleation.

The deformation behavior of Si is, however, modified by the presence of hard, brittle coatings, which provide load support to the substrate and enhance its mechanical properties by shifting the elastic–plastic behavior to higher loads.^{16–19} Cross-sectional transmission electron microscopy (XTEM) studies of diamondlike carbon (DLC) coatings on silicon substrates^{20–23} have shown that the presence of the coating alters the deformation behavior in the substrate so that, at lower loads of indentation, only slip is observed in the substrate, without any phase transformation being evident. Therefore, in such systems the initial deformation mechanism responsible for pop-ins changes from phase transformation to dislocation nucleation in the silicon substrate.

This study attempts to correlate the experimental observations described previously in the DLC coating–Si system following indentation with spherical indenters^{20,23} to the theoretically calculated stresses produced below the

^{a)}Address all correspondence to this author.
e-mail: Ayesha@materials.unsw.edu.au
DOI: 10.1557/JMR.2010.0131

indenter tip using the ELASTICA (ASMEC, Radeberg, Germany) software package.²⁴ The ELASTICA software package allows the modeling of linear elastic contact problems on multilayer coatings (up to three layers on a substrate) in a time efficient manner, without any finite element modeling (FEM). Using the elastic properties of the material, or materials, the program analytically calculates the three-dimensional stress and deformation fields during elastic contact assuming a Hertzian pressure distribution in a homogeneous isotropic material.

The theory used in the development of the ELASTICA software, together with its application to single and multilayers in the determination of the Young's modulus of coated layers, the estimation of the distribution of stresses under different loading conditions, characterization of regions of maximum Mises stresses, and prediction of the onset of plastic deformation has been discussed by the authors in several publications.^{25–30} In these prior studies, it was assumed that the Hertzian pressure distribution does not restrict the analysis because this situation is a good approximation for most of the real contact problems. For coated systems, although the presence of the coating renders the system inhomogeneous, comparisons with time-consuming finite element calculations performed by the authors of this software, have shown that the deviation of the predicted pressure distribution from a Hertzian pressure distribution is negligibly small for film-to-substrate modulus ratios between 0.125 and 8.³¹ Since the modulus ratios for the coating-substrate system used in this study are within this range, assumption of Hertzian distribution can be considered to be valid.

The ELASTICA software has also been used by several other researchers for simulating the contact deformation on layered systems. For example, Palacio et al.³² have used it to assess the load carrying ability of CN_x coatings on different substrates and Walter et al.³³ to determine the Young's modulus of the CrN thin films from the simulated load–displacement curves. Other studies^{34–37} have used ELASTICA to characterize the von Mises effective stress profiles in the coated systems to determine the critical load for the initiation of the plastic deformation in the respective coating and substrates. On the basis of these theoretical calculations and experimental data, Wanstrand et al.³⁴ proposed a surface design for a low weight machine. However, these studies did not correlate the simulation studies with experimentally observed microstructures following nanoindentation.

On the other hand, Bradby et al.¹² related the hydrostatic and shear stress in silicon to the experimental observed phase transformation and plastic deformation in Si following nanoindentation to different loads, whereas Oliver et al.³⁸ have estimated the hydrostatic and shear stress distributions in both Ge and Si films to determine the dependence of the preferred deformation

mechanism in the coating. In this study, the stresses generated in the coating, as well as the substrate, have been correlated with the experimentally observed microstructures to explain the observed change in the deformation mechanism from one of phase transformation in uncoated silicon to plastic deformation in the coated substrate.

II. EXPERIMENTAL PROCEDURE

Simulation studies were performed on two DLC coatings of 1.6 and 0.6 μm thickness deposited by a radio frequency plasma deposition technique on (100) Si substrates and uncoated (100) Si. The experimental procedure used for deposition of the coating, nanoindentation studies, and the characterization of the coatings following indentation has been discussed in detail in earlier publications.^{20–23}

A. Parameters for simulation

The elastic properties used for the ELASTICA simulation are given in Table I. The elastic modulus and Poisson's ratio for diamond were taken from the literature,^{15,39} and also the Poisson's ratio for the two coatings.^{40,41} The hardness and elastic modulus of the coatings were determined by performing nanoindentation using a Hysitron Triboindenter with a Berkovich indenter having a tip radius of 100 nm. The indenter was calibrated using a fused silica standard and the reduced elastic modulus was determined following the procedure described by Oliver and Pharr,⁴² from which the absolute elastic modulus was calculated and used for simulation.

B. Correlation with microstructure

The onset of yield in a multiaxial stress state can be adequately described by the Tresca (σ_T) shear stress and is generally used as a criterion for yielding. Furthermore, it has been suggested that for spherical indentation, it is usually sufficient to carry out the calculation only along the indentation axis, since the maximum value of σ_T is always located on the depth axis. Therefore, in this study the simulations performed along the indentation axis, Z , are discussed.

TABLE I. Elastic properties of the coatings and substrate and thickness of coatings.

Material	E-modulus (GPa)	Poisson's ratio	Thickness (μm)
Indenter	1141	0.07	
Substrate	165	0.28	Infinite
Layer 1 – 1.6- μm DLC	123	0.25	1.6
Layer 1 – 0.6- μm DLC	146	0.25	0.6

The measured hardness, of the two coatings investigated here, was found to be in the range 14.5–17.6 GPa. Schwarzer et al.⁴³ have reported that the ratio between hardness and yield strength has a characteristic value of ~ 1.6 for DLC coatings. Based on this, the magnitude of yield strength ranges from 9 to 11 GPa for these coatings. Therefore, shear stresses of the order of 11 GPa have been regarded as necessary to initiate plastic deformation within the coatings. For Si, the yield strength has been reported as 11.2 GPa from other measurements.⁴⁴ Therefore, values of this order are necessary for yield to occur. On the other hand, the hydrostatic stresses, σ_H , associated with the Hertzian stress fields beneath the indenter are reported to be responsible for phase transformations in the silicon substrate.^{6,45} The accepted value for the transformation of Si-I to Si-II under pure hydrostatic stress is of the order 11.3 to 12 GPa.^{6,45,46} However, the presence of shear stresses during indentation have been reported to lower the transformation pressure to 8 GPa.^{47,48} For example, Bradby et al.¹¹ have observed localized phase transformation beneath the indenter at a mean contact pressure of 9.9 GPa, following indentation to a load of 20 mN with a 4.2- μm -radius spherical indenter. Therefore, hydrostatic stresses above 8 GPa have been considered necessary for phase transformation in the substrate.

Based on the above discussion, the subsurface microstructural features observed in the two (0.6 and 1.6 μm) coatings following indentation to various loads are discussed in relation to the stress fields (σ_T , and σ_H) developed in the coating-substrate system for a spherical indenter with a tip radius of 5 μm . From the simulated distribution of stresses, the possibility, or otherwise, of plastic deformation in the coating and the substrate and phase transformation in the silicon substrate is predicted and compared with the observed microstructural features. An estimation of the actual distribution of the deformation and transformation zones was not attempted, since only the elastic stresses are being determined neglecting any plastic deformation within the coating, which would further alter the distribution of stresses, as well as plastic deformation and variation of properties with crystal direction in the substrate.

III. RESULTS

A. Uncoated Si

The isobaric plots of σ_T and σ_H in the XZ plane generated by the spherical indenter on (100) Si following indentation to a load of 50 mN are shown in Figs. 1(a) and 1(b), respectively. The corresponding two-dimensional (2D) plots depicting the variation of the σ_T and σ_H along a line parallel to the indentation axis are shown in Figs. 2(a) and 2(b). A maximum σ_T value of 13.41 GPa is located at a depth of $\sim 0.51 \mu\text{m}$ beneath the surface. On

FIG. 1. Simulated 2D contours of stresses generated in XZ plane of uncoated (100) Si following indentation to 50 mN (a) σ_T and (b) σ_H . The stresses shown in the contours are in GPa.

FIG. 2. Profiles of (a) σ_T and (b) σ_H along the indentation axis, Z , following indentation of (100) Si to 50 and 100 mN.

the other hand, the maximum σ_H of 18.19 GPa is situated at the surface of the sample. Although the maximum σ_T experienced by Si is higher than the value required for plastic deformation (11.2 GPa), σ_H at the surface is significantly higher than that required for phase transformation to occur. Therefore, uncoated (100) is expected to undergo phase transformation, as well as some plastic deformation, at this load. XTEM observations of (100) Si reported in literature¹⁰ clearly show evidence of phase transformation beneath the indenter tip and plastic deformation below the transformation zone following indentation to 50 mN.

Increasing the indentation load to 100 mN increases the σ_T and σ_H generated in uncoated (100) Si and also shifts the location of maximum σ_T to greater depths, as is clearly evident in the 2D-plots (Fig. 2). This results in a larger volume of transformed material, as well as plastic deformation within the Si, consistent with observations in the literature.¹⁰

B. 1.6- μm coating

The isobaric plot of σ_T in the XZ plane generated by spherical indentation on the 1.6- μm coating on (100) Si substrate following indentation to a load of 100 mN is shown in Fig. 3(a). It is seen from this figure that the region of maximum σ_T of 14.98 GPa is located at a depth of 0.66 μm beneath the indenter, i.e., within the coat-

ing. The 2D graph obtained from the stress contours [Fig. 4(a)] gives a clear representation of the variation of σ_T along the indentation axis, especially across the interface. It is evident from this plot that from a value of 6.32 GPa at the surface, the magnitude of σ_T increases with depth and reaches a maximum value at a depth of 0.66 μm within the coating. After reaching this maximum value, the stress decreases with depth within the coating to a value of 9.69 GPa at the coating-substrate interface. At this interface, when the substrate is encountered, the stress again increases slightly and reaches a maximum value of 10.07 GPa and then decreases further within the substrate. Since shear stresses of the order of 11 GPa are necessary to initiate plastic deformation in the coating and the 1.6- μm -thick coating experiences a σ_T of 14.98 GPa, the coating should exhibit plastic deformation. In contrast, the shear stress value of 10.07 GPa is below that required to initiate slip in silicon. Therefore, the substrate should not exhibit any plastic deformation at this load.

On the other hand, σ_H has a maximum value of 18.36 GPa at the surface of the coating, as shown in Figs. 3(b) and 4(b). This decreases with depth and close to the interface within the silicon substrate it has a value of 4.11 GPa, which is insufficient for phase transformation to occur. Thus, the simulation of the stress fields suggest the presence of plastic deformation only in the coating and an absence of plastic deformation or phase

FIG. 3. Simulated 2D contours of stresses (in GPa) generated in XZ plane of a 1.6- μm DLC coating; (a, c) σ_T following indentation to 100 and 150 mN, respectively; (b, d, e) σ_H following indentation to 100, 150, and 300 mN, respectively.

FIG. 4. Profiles of (a) σ_T and (b) σ_H along the indentation Z axis of the 1.6- μm DLC coating following indentation to various loads.

transformation in the substrate, at a load of 100 mN. These results agree with the experimental finding of deformation in the coating and none in the substrate, as observed in the XTEM images at this load [Fig. 5(a)], which shows localized compression of the coating beneath the indenter tip (shown by the double-ended arrow, labeled K) and only a convergence of bend contours, labeled B, in the silicon substrate without any evidence of slip or phase transformation.²⁰

Figures 3(c) and 4(a) show the Tresca shear stress contours and 2D profiles at an indentation load of 150 mN. The maximum shear stress increases to 17.29 GPa and is located at a greater depth of 0.75 μm . More importantly, the shear stress in the silicon substrate increases to 12.49 GPa, which is greater than the critical stress for initiating plastic deformation in the substrate. However, the hydrostatic stress [Figs. 3(d) and 4(b)] value of 5.63 GPa in silicon is still less than the critical stress required for transformation to occur. Based on the above, it can be predicted that the shear stresses developed in silicon are sufficient to cause plastic deformation in the coating and the silicon substrate, but the hydrostatic stress is low enough to prevent phase transformation. XTEM images [Fig. 5(b)], following indentation to 150 mN,²⁰ clearly showed plastic deformation in the coating and the substrate, without any phase transformation in the Si, consistent with the simulation results. Dislocations, labeled P,

FIG. 5. XTEM images of the 1.6- μm coating following indentation to loads of (a) 100 mN, (b) 150 mN, (c) 300 mN, and (d) 400 mN.

and planar defects, labeled Q, are evident in the silicon substrate in Fig. 5(b).

Further increases in the indentation load to still higher values, increases the magnitude of σ_T and σ_H developed in the coating-substrate system and also shifts the location of the maximum σ_T to greater depths within the sample. More importantly, for an indentation load of 300 mN, the maximum σ_H [Figs. 3(e) and 4(b)] experienced by the substrate reaches a value of 9.35 GPa, which is greater than the value required for inducing phase transformation in Si. Examination of XTEM images following indentation to 300 mN [Fig. 5(c)]²⁰ clearly shows the presence of a transformation zone, labeled X, in the silicon substrate. Further increases in load increases the magnitude of σ_H generated in the substrate, which should result in an increased volume of transformation in silicon. This is clearly evident in Fig. 5(d), which shows a large volume of the transformation zone, labeled X, in the substrate following indentation to a load of 400 mN.⁴⁹ Table II summarizes the values of σ_T at the surface of the sample, the maximum σ_T within the coating, and the depth at which this maximum is located and the maximum σ_H developed in the coating and the substrate for various applied loads, and Fig. 6 illustrates this variation.

In summary, simulation of stress fields in 1.6- μm coating indicates that indentation loads of 150 mN or more are required to initiate plastic deformation, and loads above 300 mN are necessary for inducing phase transformation in the silicon substrate. In contrast, in uncoated (100) Si the critical values of σ_T and σ_H , values required for deformation and phase transformation, respectively, are attained for indentation loads lower than

50 mN. Thus, the presence of the DLC (1.6 μm thick) coating provides load shielding of the substrate and reduces the magnitude of σ_T and σ_H transferred to the silicon substrate. Consequently, at lower loads the σ_T and σ_H values experienced by the substrate are less than

TABLE II. Simulated values of σ_T and σ_H in the coating and substrate for the 1.6- μm coating at various indentation loads.

Load (mN)	DLC coating (thickness = 1.6 μm)				Si substrate	
	Surface σ_T (GPa)	Max. σ_T (GPa)	Depth of max. σ_T (μm)	Max. σ_H (GPa)	Max. σ_T (GPa)	Max. σ_H (GPa)
100	6.32	14.98	0.67	18.36	10.07	4.11
150	7.48	17.29	0.75	21.02	12.88	5.63
200	8.45	19.13	0.82	23.16	15.15	6.99
300	10.03	22.03	0.91	26.55	18.69	9.35
400	11.44	24.3	0.98	29.26	21.44	11.41
500	12.56	26.2	1.03	31.57	23.67	13.27

FIG. 6. Variation of maximum σ_T and σ_H in the coating and substrate with indentation load for 1.6- μm DLC coating.

required for plastic deformation and phase transformation, necessitating much higher loads to observe these features.

C. 0.6- μm coating

The simulated stress fields of σ_T generated in the XZ plane of the 0.6- μm coating on (100) Si substrate following indentation to a load of 50 mN with a spherical indenter are illustrated in Fig. 7(a). The region of maximum σ_T is situated within the coating, $\sim 0.48 \mu\text{m}$ beneath the indenter tip, and has a value of 12.98 GPa. The 2D plot of σ_T along the indentation axis [Fig. 8(a)] clearly depicts this variation in σ_T across the interface. Similar to results on the thicker (1.6 μm) coating, after reaching the maximum within the coating, σ_T decreases to 12.72 GPa on moving closer to the interface. However, the magnitude of this decrease is clearly less than that observed in the thicker coating (1.6 μm thick), presumably because of its lower thickness as compared to the thicker coating. Again, at the coating-substrate interface, there is a further decrease in σ_T to 12.25 GPa, after which the stress decreases in a continuous manner within the substrate. Since the maximum σ_T experienced by the coating (12.98 GPa) and the substrate (12.25 GPa) are larger than the critical stresses required respectively for plastic deformation, both the coating and the silicon substrate are expected to deform on indentation to this load.

The magnitude of σ_H [Figs. 7(b) and 8(b)], on the other hand, decreases from a maximum value of 16.29 GPa at the surface of the coating to 7.11 GPa at the interface, where it increases slightly to 7.41 GPa before decreasing continuously with depth. The maximum value of σ_H experienced by the substrate (7.41 GPa) is insufficient for phase transformation to occur at this load. These

FIG. 7. Simulated 2D contours of stresses (in GPa) generated in XZ plane of 0.6- μm DLC coating system; (a, c) σ_T following indentation to 50 and 100 mN, respectively; (b, d) σ_H following indentation to 50 and 100 mN, respectively.

FIG. 8. Profiles of (a) σ_T and (b) σ_H along the indentation Z axis of the 0.6- μm DLC coating following indentation to various loads.

FIG. 9. XTEM images of the 0.6- μm coating following indentation to (a) 50 mN, (b) 100 mN, (c) 150 mN, and (d) 200 mN.

predictions clearly match the experimental observation [Fig. 9(a)] of only plastic deformation in the coating, labeled K, as well as plastic deformation, i.e., slip bands, labeled P, within the substrate, without any evidence of phase transformation.²³

With an increase in the indentation load to 100 mN, the maximum σ_T within the coating and in the substrate increases to 16.35 and 15.68 GPa, respectively [Figs. 7(c) and 8(a)], suggesting that the extent of plastic deformation should increase both in the coating and the substrate. However, the stress distribution experienced by the coating and the substrate differs only slightly from that observed at the lower load of 50 mN, which is evident in Fig. 8(a). The decrease in σ_T in the coating after reaching the maximum stress is marginally lower, whereas the decrease of σ_T at the interface and the increase within the substrate are higher. In contrast, the variation in σ_H [Figs. 7(d) and 8(b)] along the indentation axis is similar to that calculated for the lower load; only the magnitudes are higher. The maximum σ_H developed in the substrate is about 11.15 GPa, sufficient for the initiation of phase transformation in Si. These predictions are consistent with the observation of a phase transformation zone (labeled X) as well as increased plastic deformation in the substrate at an indentation load of 100 mN [Fig. 9(b)], as compared to the lower load of 50 mN.²³

With further increases in the indentation load, σ_T and σ_H generated in the coating and substrate increase further resulting in increased deformation in both regions, and an increased volume of phase transformation in the substrate. This is consistent with the observed XTEM images [Figs. 9(c) and 9(d)].²³ The variation of these stresses with indentation load are shown in Table III and Fig. 10.

For the thinner coating also, comparison of the stress fields generated on indentation to 50 mN with those of (100) Si indented to the same load reveals that uncoated silicon experiences values of σ_H at the surface, sufficient for initiating phase transformation, whereas a 0.6- μm -thick DLC coating on a Si substrate provides load support and reduces the hydrostatic stresses experienced by the silicon substrate to values less than those required for phase transformation. An increase in the indentation load to 100 mN, however, increases the hydrostatic stress to values sufficient to initiate phase transformation. XTEM images of the 0.6- μm coating following indentation to various loads support these experimental observations. However, as compared to the thicker coating, significantly lower loads are required to observe these features, confirming that thinner coatings provide lower load support to the substrate than a thicker coating, consistent with the observations in literature.^{17,50}

Furthermore, similar to the simulation results on the thicker coating (Table II), the location of maximum σ_T in the thinner coating (Table III) increases with depth, however to a much smaller extent. In contrast, unlike the 1.6- μm coating, where the maximum σ_T generated in the substrate is always located at the interface, for the 0.6- μm -thick coating, the location of maximum σ_T in the substrate increases to larger depths beneath the indenter with an increase in load.

TABLE III. Simulated values of σ_T and σ_H in the coating and substrate for the 0.6- μm coating for various indentation loads.

Load (mN)	DLC coating (thickness = 0.6 μm)				Si substrate		
	Surface σ_T (GPa)	Max. σ_T (GPa)	Depth of max. σ_T (μm)	Max. σ_H (GPa)	Max. σ_T (GPa)	Depth of max. σ_T (μm)	Max. σ_H (GPa)
50	5.53	12.98	0.48	16.29	12.25	0.60	7.41
100	7.15	16.35	0.59	20.57	15.68	0.70	11.15
150	8.30	18.63	0.599	23.58	18.08	0.80	13.95
200	9.22	20.32	0.5994	25.98	20.00	0.87	16.28

FIG. 10. Variation of maximum σ_T and σ_H in the coating and the substrate for 0.6- μm coating.

IV. DISCUSSION

As mentioned earlier, ELASTICA simulates only linear elastic contact problems and plastic deformation in the coating and the substrate is neglected. According to Wanstrand et al.,³⁴ although plastic flow, if present, would change the stress distribution outside the plastic zone, such calculations (using ELASTICA) can still be used to predict the combination of contact geometry and the load for which plastic flow will be initiated. In this study, although plastic deformation was observed in the coating and the substrate, from the theoretically calculated shear and hydrostatic stresses (using ELASTICA simulation), the observed change in the deformation mechanism of the substrate in the presence of the overlying coating has been justified.

Here, we attempt to correlate the other observation of a wider distribution of the plastic zone in the substrate in the presence of the coating. If the σ_T contours obtained for the 1.6- μm -thick coating at 150 mN [Fig. 3(c)] are compared with those obtained for (100) Si at 50 mN [Fig. 1(a)], it is evident that, in the case of the coating, the σ_T is distributed over a much wider area of the substrate. By comparing the stress distribution within the substrate parallel to the surface, it is possible to quantify the width of the stress distribution as follows: from the distribution of σ_T parallel to the indentation axis, i.e., along the Z axis at a particular indentation load, the depth at which uncoated Si attains the maximum value is first located (e.g., a depth of 0.51 μm for 50 mN load). The distribution of the σ_T parallel to the surface,

FIG. 11. σ_T profiles along an axis parallel to the sample surface (radial direction) at a depth of 0.5 μm beneath the surface where σ_T is maximum in uncoated (100) Si (dotted line) on indentation to 50 mN and in 1.6- μm coating system at the interface, on indentation to 150 mN.

i.e., along the radial axis, X, is then plotted for uncoated silicon at this depth of maximum σ_T . A similar procedure is followed for the coating after locating the depth at which the substrate attains a maximum value of σ_T . In the case of the 1.6- μm coating, this occurs at the interface.

Figure 11 shows the variation of σ_T parallel to the radial axis for uncoated silicon indented to 50 mN (shown as a dotted line) and the 1.6- μm DLC coated system indented to 150 mN (shown as a solid line) at the location along the indentation axis where σ_T has the maximum value in Si. From these plots, it is possible to determine the zone along the X axis (i.e., parallel to the surface) where the stress values are greater than the critical σ_T needed for yielding. For example, from Fig. 11, it can be seen that for Si indented to 50 mN, σ_T values are higher than the critical value of 11.2 GPa, between X values of -0.74 to $+0.74$ μm (distance pq). Therefore, it can be inferred that the maximum σ_T extends to a width of 1.48 μm at a depth of 0.5 μm beneath the indenter tip. A similar calculation for the 1.6- μm coating [Fig. 11(b)], yields a width (p'q') of 1.8 μm , at the interface, at a load of 150 mN. Similar calculations for other loads are shown in Table IV, which gives a comparison of the widths in the radial direction (i.e., parallel to the surface) over which the σ_T , above the critical value for deformation, extends in the Si substrate of the coating

TABLE IV. Maximum σ_T experienced by the substrate at various loads, depth of maximum σ_T in the substrate and the width over which σ_T exceeds the critical value for deformation (at this depth) calculated for 1.6- and 0.6- μm coatings and the corresponding parameters for (100) Si at comparable values of σ_T .

Stress experience in uncoated (100) Si				Stress experienced by the Si substrate in the coating composite				
				0.6 μm coating		1.6 μm coating		
Load (mN)	Max. σ_T (GPa)	Depth of max. σ_T (μm)	Width (μm)	Max. σ_T (GPa)	Width (μm)	Load (mN)	Max. σ_T (GPa)	Width (μm)
50	13.22	0.51	1.48	12.25	1.13	150	12.88	1.80
100	16.66	0.64	2.50	15.68	2.39	200	15.15	2.90
150	19.07	0.73	3.12	18.08	3.07	300	18.69	4.13
200	20.99	0.81	3.63	20.00	3.61	400	21.44	4.92

system (maximum σ_T is at the interface) with the corresponding parameters for uncoated (100) Si, for comparable σ_T values. The spread of maximum σ_T for uncoated Si and the substrate for the 1.6- μm coating at comparable values of σ_T are also plotted in Fig. 12. It is evident from Table IV and Fig. 12 that the distribution of σ_T in Si, parallel to the surface, when coated with a 1.6- μm -thick coating, is significantly larger than in uncoated Si. Furthermore, Fig. 12 also shows that not only is the width of σ_T in Si larger for the 1.6- μm coating, but this difference in the widths of σ_T increases with the maximum experienced σ_T , or in other words, with increase in the indentation load. These results are in agreement with the experimental observation of plastic deformation over a wider region of the substrate parallel to the interface in the 1.6- μm coatings.²⁰ However, as summarized in Table V, the extensive deformation parallel to the interface experimentally observed in the XTEM images^{20,49} is greater than the values obtained by simulation. This is possibly because ELASTICA takes into account only elastic deformation, whereas extensive plastic deformation ($\sim 11\%$ compressive strain at 400 mN) observed in the 1.6- μm coating and in the substrate would lead to further alteration in the stress distribution within the substrate, giving rise to the observed extensive plastic deformation parallel to the interface. To take into account the observed plastic deformation in the coating and the substrate, techniques such as FEM and the boundary element method could also be used. However, these modeling studies are time-consuming and beyond the scope of this study, whereas ELASTICA modeling allows a rapid calculation of the stresses that can explain the experimental findings.

For the thinner coating, comparison of the σ_T contours, with those obtained for (100) Si at an indentation load of 50 mN, shows that the distribution of σ_T parallel to the surface is comparable. Quantification of the width of maximum σ_T stress distribution, carried out following the procedure given above, is also summarized in Table IV. From this table, it appears that the calculated values of the width of σ_T in the substrate of 0.6- μm coating are slightly lower than those of uncoated Si. This

FIG. 12. Plot of the width along the radial direction where σ_T in the substrate exceeds the critical value for deformation against the maximum σ_T experienced for uncoated (100) Si and 1.6- and 0.6- μm coatings at comparable values of σ_T in the substrate.

TABLE V. Extent of deformation parallel to the interface obtained from simulation and experiments for the 1.6- μm coating.

Load (mN)	Width of deformation in substrate (μm)	
	Simulation	Experimental
150	1.80	2
200	2.90	3.5
300	4.13	4.6
400	4.92	5.8

is because the corresponding magnitudes of the stresses are also lower. However, if these values are plotted (Fig. 11), it can be seen that, at comparable stresses, the curve for the substrate of 0.6- μm coating is higher than that of uncoated Si, and this difference increases with indentation load, indicating that the substrate of 0.6- μm coating should exhibit slightly higher widths of plastic deformation parallel to the interface compared to uncoated Si, particularly at higher loads. Examination of XTEM images following indentation also reveals that for comparable depths of deformation the widths of plastic deformation parallel to the interface are higher for the substrate with a coating, particularly at higher loads. Similar to observations on the 1.6- μm coating, the XTEM

TABLE VI. Extent of deformation parallel to the interface obtained from simulation and experiments for the 0.6- μm coating.

Load (mN)	Width of deformation in substrate (μm)	
	Simulation	Experimental
50	1.13	1.7
100	2.39	2.2
150	3.07	3.8
200	3.61	3.86

images of the 0.6- μm coating²³ show a much wider distribution of plastic deformation, as well as phase transformation, than that indicated from the simulation calculations (Table VI). This is again because plastic deformation, which was observed within the coating, has been neglected in the simulation studies. Simulation studies involving FEM may take this into account, but are more time-consuming. However, for the 100 mN load, the experimentally measured widths of deformation appear to be lower than the simulated values, possibly due to the TEM cross section not being exactly at the center of the indentation. Furthermore, comparison of data for the two coatings (Table IV) show that the distribution of σ_T parallel to the interface for the 0.6- μm coating is significantly lower than that for the thicker coating. These results are consistent with XTEM observations of extensive deformation parallel to the interface for the 1.6- μm coating,²⁰ as compared to the 0.6- μm coating.²³ We have shown that the ELASTICA simulations generated here correlate well to experimental observations on DLC-coated silicon. It is likely this approach could be successfully extrapolated to more complex DLC-based coatings.^{51,52}

V. CONCLUSIONS

Simulation studies show that in uncoated silicon the hydrostatic stresses developed beneath the indenter are significantly higher than the shear stresses, consistent with observations that phase transformation is the dominant deformation mechanism. The presence of the DLC coating above Si provides load shielding and alters the distribution of stresses experienced by the substrate, lowering both the hydrostatic and the shear stresses. However, the reduction in hydrostatic stress is larger than that in shear stress, so much so that the hydrostatic stresses are reduced to values less than that required for phase transformation, thus making shear as the probable mode of deformation.

The magnitude and distribution of the shear and hydrostatic stresses in the substrate were found to depend on the indentation load and the thickness of the coating. Accordingly, the thinner (0.6 μm thick) coating exhibited the critical shear stress for onset of yielding and the hydrostatic stress required for phase transformation at lower loads (50 and 100 mN, respectively) as compared

to the thicker (1.6 μm thick) coating, in which the Tresca shear stress and hydrostatic stresses exceeded the critical values for onset of yielding and phase transformation at higher indentation loads of 150 and 300 mN, respectively. These calculations correlated well with the observed sub-surface microstructures of the residual indents.

The width of plastic deformation parallel to the interface was found to increase with the thickness of the coating. The significant increase in the width of plastic deformation in the substrate parallel to the interface that was observed in the case of the 1.6- μm -thick coating as compared to uncoated Si was also correlated to the wider distribution of Tresca shear stress in the substrate.

REFERENCES

1. D.R. Clarke, M.C. Kroll, P.D. Kirchner, R.F. Cook, and B.J. Hockey: Amorphization and conductivity of silicon and germanium induced by indentation. *Phys. Rev. Lett.* **60**, 2156 (1988).
2. G.M. Pharr, W.C. Oliver, and D.R. Clarke: Hysteresis and discontinuity in the indentation load-displacement behavior of silicon. *Scr. Metall.* **23**, 1949 (1989).
3. G.M. Pharr, W.C. Oliver, and D.S. Harding: New evidence for a pressure-induced phase transformation during the indentation of silicon. *J. Mater. Res.* **6**, 1129 (1991).
4. T. Page, W.C. Oliver, and C.J. McHargue: The deformation behavior of ceramic crystals subjected to very low load (nano)indentations. *J. Mater. Res.* **7**, 450 (1992).
5. D.L. Callahan and J.C. Morris: The extent of phase transformation in silicon hardness indentations. *J. Mater. Res.* **7**, 1614 (1992).
6. E.R. Weppelmann, J.S. Field, and M.V. Swain: Observation, analysis, and simulation of the hysteresis of silicon using ultramicro-indentation with spherical indenters. *J. Mater. Res.* **8**, 830 (1993).
7. T.F. Page, L. Riester, and S.V. Hainsworth: The plasticity response of 6H-SiC and related isostructural materials to nanoindentation: Slip versus densification, in *Fundamentals of Nanoindentation and Nanotribology*, edited by N.R. Moody, W.W. Gerberich, N. Burnham, and S.P. Baker (Mater. Res. Soc. Symp. Proc. **522**, Warrendale, PA, 1998), p. 113.
8. A. Kailer, Y.G. Gogotsi, and K.G. Nickel: Phase transformations of silicon caused by contact loading. *J. Appl. Phys.* **81**, 3057 (1997).
9. V. Domnich, Y. Gogotsi, and S. Dub: Effect of phase transformations on the shape of the unloading curve in the nanoindentation of silicon. *Appl. Phys. Lett.* **76**, 2214 (2000).
10. I. Zarudi and L.C. Zhang: Structure changes in monocrystalline silicon subjected to indentation-experimental findings. *Tribol. Int.* **32**, 701 (1999).
11. J.E. Bradby, J.S. Williams, J. Wong-Leung, M.V. Swain, and P. Munroe: Transmission electron microscopy observation of deformation microstructure under spherical indentation in silicon. *Appl. Phys. Lett.* **77**, 3749 (2000).
12. J.E. Bradby, J.S. Williams, J. Wong-Leung, M.V. Swain, and P. Munroe: Mechanical deformation in silicon by micro-indentation. *J. Mater. Res.* **16**, 1500 (2001).
13. S.J. Lloyd, J.M. Molina-Aldareguia, and W.J. Clegg: Deformation under nanoindenters in Si, Ge, and GaAs examined through transmission electron microscopy. *J. Mater. Res.* **16**, 3347 (2001).
14. A.J. Whitehead and T.F. Page: Nanoindentation studies of thin film coated systems. *Thin Solid Films* **220**, 277 (1992).
15. D. Lorenz, A. Zeckzer, U. Hilpert, P. Grau, H. Johanson, and H.S. Leipner: Pop-in effect as homogeneous nucleation of

- dislocations during nanoindentation. *Phys. Rev. B: Condens. Matter* **67**, 172101 (2003).
16. J.C. Knight, A.J. Whitehead, and T.F. Page: Nanoindentation experiments on some amorphous hydrogenated carbon (a -C:H) thin films on silicon. *J. Mater. Sci.* **27**, 3939 (1992).
17. S.V. Hainsworth, T. Barlett, and T.F. Page: The nanoindentation response of systems with thin hard carbon coatings. *Thin Solid Films* **236**, 214 (1993).
18. T.F. Page and S.V. Hainsworth: Using nanoindentation techniques for the characterization of coated systems: A critique. *Surf. Coat. Technol.* **61**, 201 (1993).
19. E.G. Berasategui and T.F. Page: The contact response of thin SiC-coated silicon systems-characterization by nanoindentation. *Surf. Coat. Technol.* **163–164**, 491 (2003).
20. A.J. Haq, P.R. Munroe, M. Hoffman, P.J. Martin, and A. Bendavid: Nanoindentation-induced deformation behavior of diamond-like carbon coatings on silicon substrates. *Thin Solid Films* **515**, 1000 (2006).
21. A.J. Haq, P.R. Munroe, M. Hoffman, P.J. Martin, and A. Bendavid: Deformation behavior of DLC coatings on (111) silicon substrates. *Thin Solid Films* **516**, 267 (2006).
22. A.J. Haq, P.R. Munroe, M. Hoffman, P.J. Martin, and A. Bendavid: Berkovich indentation of diamondlike-carbon coatings on silicon substrates. *J. Mater. Res.* **23**, 1862 (2008).
23. A.J. Haq, P.R. Munroe, M. Hoffman, P.J. Martin, and A. Bendavid: Effect of coating thickness on the deformation behavior of diamond-like carbon (DLC)–Si system. *Thin Solid Films* **518**, 2021 (2010).
24. T. Chudoba and N. Schwarzer: ELASTICA software package version 3, <http://www.asmec.de/>.
25. N. Schwarzer, M. Whittling, M. Swain, and F. Richter: The analytical solution of the contact problem of spherical indenters on layered materials: Application for the investigation of TiN films on silicon. *Thin Solid Films* **270**, 371 (1995).
26. N. Schwarzer, T. Chudoba, D. Billep, and F. Richter: Investigation of coating substrate compounds using inclined spherical indentation. *Surf. Coat. Technol.* **116–119**, 244 (1999).
27. N. Schwarzer, F. Richter, and G. Hecht: The elastic field in a coated half-space under Hertzian pressure distribution. *Surf. Coat. Technol.* **114**, 292 (1999).
28. N. Schwarzer: Arbitrary load distribution on a layered half space. *J. Tribol.* **122**, 673 (2000).
29. T. Chudoba, N. Schwarzer, F. Richter, and U. Beck: Determination of mechanical film properties of a bilayer system due to elastic indentation measurements with a spherical indenter. *Thin Solid Films* **377–378**, 366 (2000).
30. T. Chudoba, N. Schwarzer, V. Linss, and F. Richter: Determination of mechanical properties of graded coatings using nanoindentation. *Thin Solid Films* **469–470**, 239 (2004).
31. T. Chudoba and N. Schwarzer: ELASTICA software package version 3 help manual, http://www.siomec.de/downloads/Elastica_Help.pdf.
32. J.F. Palacio, S.J. Bull, J. Neidhardt, and L. Hultman: Nano-indentation response of high performance fullerene-like CN_x . *Thin Solid Films* **494**, 63 (2006).
33. C. Walter, T. Antretter, R. Daniel, and C. Mitterer: *Surf. Coat. Technol.* **202**, 1103 (2007).
34. O. Wanstrand, A.E. Kassman-Rudolphi, and S. Hogmark: Design of low weight components: A theoretical approach. *Surf. Eng.* **18**, 93 (2002).
35. O. Wanstrand, N. Schwarzer, T. Chudoba, and A.E. Kassman-Rudolphi: Load carrying capacity of Ni plated media in spherical indentation: Experimental and theoretical results. *Surf. Eng.* **18**, 98 (2002).
36. G.A. Fontalvo, R. Daniel, and C. Mitterer: Interlayer thickness influence on the tribological response of bi-layer coatings. *Tribol. Int.* **43**, 108 (2010).
37. N. Fujisawa, D.R. McKenzie, N.L. James, J.C. Woodard, and M.V. Swain: Combined influences of mechanical properties and surface roughness on the tribological properties of amorphous carbon coatings. *Wear* **260**, 62 (2006).
38. D.J. Oliver, J.E. Bradby, J.S. Williams, M.V. Swain, and P. Munroe: Thickness-dependent phase transformation in nano-indented germanium thin films. *Nanotechnology* **19**, 475709 (2008).
39. T. Malkow, I. Arce-Garcia, A. Kolitsch, D. Schneider, S.J. Bull, and T.F. Page: Mechanical properties and characterisation of very thin CN_x films synthesised by IBAD. *Diamond Relat. Mater.* **10**, 2199 (2001).
40. X. Li and B. Bhushan: Evaluation of fracture toughness of ultra-thin amorphous carbon coatings deposited by different deposition techniques. *Thin Solid Films* **355–356**, 330 (1999).
41. B. Bhushan: Chemical, mechanical and tribological characterization of ultra-thin and hard amorphous carbon coatings as thin as 3.5 nm: Recent developments. *Diamond Relat. Mater.* **8**, 1985 (1999).
42. W.C. Oliver and G.M. Pharr: An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* **7**, 1564 (1992).
43. N. Schwarzer, T. Chudoba, and G.M. Pharr: On the evaluation of stresses in coated materials during nanoindentation with sharp indenters. *Surf. Coat. Technol.* **200**, 4220 (2006).
44. T. Chudoba, N. Schwarzer, and F. Richter: Steps towards a mechanical modeling of layered systems. *Surf. Coat. Technol.* **154**, 140 (2002).
45. J.S. Field and M.V. Swain: A simple predictive model for spherical indentation. *J. Mater. Res.* **8**, 297 (1993).
46. J.Z. Hu, L.D. Merkle, C.S. Menoni, and I.L. Spain: Crystal data for high-pressure phases of silicon. *Phys. Rev. B: Condens. Matter* **34**, 4679 (1986).
47. M.C. Gupta and A.L. Ruoff: Static compression of silicon in the [100] and in the [111] directions. *J. Appl. Phys.* **51**, 1072 (1980).
48. J.J. Gilman: Shear-induced metallization. *Philos. Mag. B* **67**, 207 (1993).
49. A.J. Haq: Deformation behavior of diamond-like carbon coatings on silicon substrates. Ph.D. Thesis, University of New South Wales, Sydney, Australia (2008).
50. B.D. Beake and S.P. Lau: Nanotribological and nanomechanical properties of 5–80 nm tetrahedral amorphous carbon films on silicon. *Diamond Relat. Mater.* **14**, 1535 (2005).
51. D. Galvan, Y.T. Pei, and J.Th.M. De Hosson: Deformation and failure mechanism of nano-composite coatings under nano-indentation. *Surf. Coat. Technol.* **200**, 6718 (2006).
52. C.Q. Chen, Y.T. Pei, K.P. Shaha, and J.Th.M. De Hosson: Nano-scale deformation mechanism of TiC/ a -C nanocomposite thin films. *J. Appl. Phys.* **105**, 114314 (2000).