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Journal

Surface science, 227

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Publication Date

1990-09-01

Center for Advanced Materials

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November 1989

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Analysis of the Interface of Hydrogenated Amorphous Carbon Films on Silicon by Angle-Resolved X-ray Photoelectron Spectroscopy

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Abstract

Thin amorphous hydrogenated carbon films were deposited from a methane r.f. plasma (13.56 MHz) at 68 mTorr on Si(100) substrates both on the powered (negatively self biased) and on the nonpowered (grounded) electrode. The interface was analyzed with angle-resolved X-ray photoelectron spectroscopy. An approximately stoichiometric silicon carbide layer was found at the interface of a hard carbon film produced on the powered electrode. The thickness of the interfacial carbide as estimated from the angle resolved spectra was approximately 7 Å, which is much thinner than previously reported by other workers. There was no interfacial silicon carbide formation evident for a soft polymer-like film produced on the grounded electrode. Instead, a submonolayer amount of oxide was detected at the interface of the soft carbon film which showed poor adhesion. Our results indicate that the high energy ions incident on the powered electrode in the r.f. plasma are responsible for the production of the interfacial silicon carbide and

are also likely responsible for the good adhesion of the film to the silicon substrate.

1 INTRODUCTION

Hydrogenated amorphous carbon (a-C:H) films can be produced by plasma assisted chemical vapor deposition with properties such as high hardness (30 GPa) which are most desirable in the area of hard film coatings¹⁾. In a recent study, we uncovered the different roles of ions and radicals in the plasma for the formation of a-C:H films of superior mechanical properties²⁾. Ions act as a structural modifier making the film harder and stronger, while radicals act primarily as the source for the deposition of polymeric species providing the bulk mass of the film.

The characterization of the interface between the film and the substrate is most important for the potential applications of a-C:H films as protective coatings. Hard a-C:H films produced under high energy ion impact exhibit a large compressive stress of several GPa, so good adhesion to the substrate is a prerequisite to prevent delamination. The films exhibit especially good adhesion characteristics when deposited on sin-

gle crystal silicon substrates. A hard a-C:H film more than 2 μm thick is easily grown on silicon without any delamination, and the films are not noticeably damaged nor delaminated by an 830 g load in a scratch adhesion test. This strong adhesion of a-C:H films on silicon suggests that the films are bound to silicon by strong chemical bonds, and that a silicon carbide layer is likely to be present at the interface.

Koidl and coworkers have used depth profiling with argon ion sputtering in their XPS and AES study to identify the interfacial carbide³⁾. They proposed a carbide layer extending over nearly a hundred angstrom, not only for hard a-C:H films on silicon, but also for soft polymer-like films that showed poor adhesion. However, high energy ion depth profiling could induce a structural change of the material being studied and alter the interfacial properties by means of the mixing that occurs as a result of the strong forward momentum transfer from the sputtering ions to target atoms.

In this paper, we present the results of an XPS analysis of the silicon-carbon film interface without the use of ion sputtering. The a-C:H films

studied in this work were deposited to thicknesses where the XPS signal originating from the interface region still contributed significantly to the overall spectrum. Due to the short mean free path of the photoelectrons, the contribution of surface (or interface) atoms can be enhanced relative to the underlying substrate by changing the angle of collection of the photoelectrons. We confirm the existence of silicon carbide at the interface of a hard a-C:H film grown on silicon. However, the thickness of the carbide as determined from angle-resolved spectra was much smaller than that reported by Koidl and coworkers. Moreover, there was no carbide formation evident at the interface of a soft polymer-like film on silicon. Plasma ion bombardment during a-C:H deposition contributes to strong adhesion by inducing the formation of an interfacial carbide layer.

2 EXPERIMENTAL

The a-C:H films were deposited in a 13.56 MHz r.f. plasma chamber from pure methane with a parallel electrode configuration as described

elsewhere²⁾. Modifications were made so that the chamber could accommodate a vacuum transfer vessel (Perkin Elmer model 04-110). After deposition the sample was first transferred to the vessel, and then to the XPS system (Perkin Elmer PHI 5300). Thus the a-C:H films were prevented from being exposed to the atmosphere before the XPS analysis. Single crystal Si(100) wafers were first etched in a 49 percent HF solution for 5 minutes and mounted on a conductive flat specimen holder (Perkin Elmer model 190) to ease the sample transfer procedure. The holder was placed on the lower electrode in the main plasma chamber. The gap distance between the substrate surface and the upper electrode was 1 cm in this configuration. After etching, the exposure time of the substrates to the atmosphere was typically less than 5 minutes after which the chamber was pumped down to a base pressure of less than 10 mTorr.

An r.f. power of 50W and a preignition methane pressure of 65 mTorr was used in the deposition of these films. Upon ignition the gas pressure rose to 68 mTorr. A hard a-C:H film was deposited at the lower electrode

by powering the lower electrode and grounding the upper electrode. A soft polymer-like film was produced, also at the lower electrode, by powering the upper electrode and grounding the lower one. The deposition time in this experiment was varied from 5 to 40 sec. The average growth rate, as deduced from the thickness-deposition time relationship measured with a profilometer for much longer deposition times, was about 1.2 Å/s for the hard a-C:H film and 0.6 Å/s for the soft polymer-like film.

The XPS spectra were taken with Mg K α radiation of 1253.6 eV. Rotation of the specimen holder allowed the electron takeoff angle to be varied from 60° to 15° with respect to the surface plane. The angle between the X-ray and the emitted electrons collected by the energy analyzer was fixed at 45°, so that the angular dependence of photoelectric emission cross section did not affect the angle-resolved XPS spectra.

3 RESULTS and DISCUSSION

3.1 XPS Studies

To analyse interfacial composition, XPS spectra in the regions of interest were taken as a function of takeoff angle for a series of short deposition times. Fig.1 shows the silicon 2p spectra at two of the takeoff angles (60° and 15°) for 0 s, 5 s, and 20 s deposition times on the powered electrode, where a hard (about 30 GPa) a-C:H film is produced. The uppermost two spectra, corresponding to zero a-C:H deposition time, were taken with a control substrate that had received identical treatment as other samples excluding plasma ignition. These control Si 2p spectra did not exhibit any oxide peak even near the grazing takeoff angle of 15° . Furthermore the peak shape was identical with that for spectra obtained with silicon wafers that had been first etched in HF and further sputter cleaned by argon ions. Oxide formation on the HF treated silicon wafers from exposure to background gases in the plasma chamber, therefore, can be ruled out.

The hard a-C:H deposition on silicon introduced a higher binding en-

ergy shoulder in the Si 2p spectra. The intensity of this shoulder relative to the pure Si 2p peak increased as the photo-electron take-off angle was reduced (see Fig.1). Fig.1 also shows the results of a computer-assisted separation of the Si 2p spectra into two overlapping peaks, i.e., a pure Si 2p peak due to the substrate bulk, and a higher binding energy component associated with the interface. A set of curve fitting parameters for the pure Si 2p signal from the substrate were obtained by analyzing the control spectra of films with no a-C:H deposited. These parameters were used in the peak separation of spectra where secondary interfacial contributions were present.

It can be seen in Fig.1 that the intensity ratio of the higher binding energy peak to the pure Si 2p peak depends strongly on the electron takeoff angle, but not on the deposition time in the range longer than 5 s (see also Fig.5). The deposition time, however, strongly affects the absolute intensity of the Si 2p signal. The angular dependance shows that the higher binding energy peak is associated with the Si atoms nearest the surface, ie., the silicon atoms at the substrate-film interface.

The independence of the intensity ratio and the decline of the absolute intensity with deposition times greater than 5 seconds, indicates that the interface formation is likely completed in the early seconds and is simply being covered up by a-C:H during the seconds thereafter.

The interfacial peak maxima were found between 100 and 101 eV, in agreement with the chemical shift of Si 2p state in silicon carbide reported by Wheeler and Pepper⁴⁾. The identification of the interfacial layer as silicon carbide is supported by the concurrent change of C 1s spectra as shown in Fig.2. These spectra can be also separated into two overlapping peaks, one associated with the deposited a-C:H and a secondary peak at lower binding energy. The curve fitting parameters for the non-interfacial C 1s signal were obtained from a spectrum taken of an a-C:H film deposited for more than 40 s, where the interfacial contribution to the spectrum is negligible. The maximum of the peak associated with the interface is at 283 eV, as expected for silicon carbide^{3,4)}.

Information about the stoichiometry of the interfacial carbide can be

extracted from the intensity ratios of the Si and C signals associated with the interface. Fig.3 shows a linear relationship between the peak areas of the Si 2p and C 1s signals that we have attributed to the interfacial carbide. The data were collected for various deposition times and takeoff angles. The line drawn in Fig.3 with a slope of unity illustrates how closely the data fits a 1:1 intensity ratio. The sensitivity factors of the PHI 5300 XPS system for Si 2p and C 1s electrons are both equal to 0.25. Also, the elastic mean free paths of photoelectrons in the a-C:H overlayer are expected to be about the same for the two peaks, because the difference in electron kinetic energy, 970 eV for C 1s vs. 1155 eV for Si 2p, should cause only about a 10 percent difference in the mean free path⁴⁾. As a result, the area intensity ratio of Si 2p to C 1s of approximately 1:1 implies that an approximately stoichiometric silicon carbide has been formed at the interface.

In addition to Si 2p and C 1s, our XPS spectra exhibited also noticeable O 1s intensity. Nonstoichiometric silicon oxide can also cause a higher binding energy shoulder in Si 2p spectra.⁴⁾ However, the good

correlation between the Si 2p and C 1s spectra in terms of chemical shift and peak area excludes any significant contribution from such oxide. Fig.4 shows spectra in the regions of O 1s, Si 2s, and Si 2p peaks, which also demonstrates irrelevance of the oxygen to the higher binding energy Si 2p shoulder. Si related peaks are almost completely attenuated at a low takeoff angle of 15° . O 1s intensity (the peak binding energy was between 531 and 532 eV) and its angle dependence varied from sample to sample, but in a typical case shown in Fig.4, the O 1s peak does not suffer any significant intensity change as a function of takeoff angle. The PHI sensitivity factor for the O 1s state is 0.66, greater by factor of 2.6 than that for the Si 2p state. If the higher binding energy component in the Si 2p spectra was due to a suboxide of silicon, the O 1s signal in Fig.4 would have to originate entirely from the interface. The insensitivity of the O 1s peak intensity to takeoff angle excludes this possibility. The oxygen is probably due primarily to a small residual bulk and/or surface contamination of the a-C:H films.

The effective thickness of the interfacial carbide can be estimated

from the angle dependence of the ratio of the interfacial Si 2p intensity to the pure Si 2p intensity from the substrate bulk, based on the relevant intensity attenuation equations⁴). In the presence of an a-C:H overlayer of thickness d_o and an interfacial carbide of thickness d_i , the pure Si 2p intensity from the silicon substrate at takeoff angle θ can be described as $I_s(\theta)$, where

$$I_s(\theta) = I_\theta \lambda_s \rho_s \exp\left(\frac{-d_i}{\lambda_i \sin\theta}\right) \exp\left(\frac{-d_o}{\lambda_o \sin\theta}\right) \quad (1)$$

and λ_s , λ_i , and λ_o are the elastic mean free paths in the silicon, the interfacial carbide, and the a-C:H overlayer, respectively, and ρ_s represents the density of Si in the substrate. The factor I_θ in Eq. (1) accounts for the photoelectric emission cross section and the angle and energy dependent instrument factor. The Si 2p intensity associated with the interfacial carbide is

$$I_i(\theta) = I_\theta \lambda_i \rho_i [1 - \exp\left(\frac{-d_i}{\lambda_i \sin\theta}\right)] \exp\left(\frac{-d_o}{\lambda_o \sin\theta}\right) \quad (2)$$

where ρ_i expresses the density of Si in the interfacial carbide. From Eq. (1) and Eq. (2) the ratio of Si2p intensity from interfacial silicon carbide to Si2p intensity from the silicon substrate is given by

$$I_i(\theta)/I_s(\theta) = \frac{\lambda_i \rho_i}{\lambda_s \rho_s} [\exp(\frac{d_i}{\lambda_i \sin \theta}) - 1] \quad (3)$$

which is independent of the parameters relating to the a-C:H overlayer as expected. Eq. (3) can be rewritten in a more convenient form like:

$$R(\theta) \equiv \ln(1 + \frac{\lambda_s \rho_s I_i(\theta)}{\lambda_i \rho_i I_s(\theta)}) = (d_i/\lambda_i)(1/\sin \theta). \quad (4)$$

Thus by plotting $R(\theta)$ as a function of $1/\sin \theta$, one can determine the interfacial carbide thickness d_i from the slope d_i/λ_i . The unknown parameters are ρ_i and λ_i , which are for the interfacial carbide. Fig.3 suggests the formation of approximately stoichiometric silicon carbide, so we use the parameters for a single crystal SiC as a first approximation. Then $\rho_s = 2.33 \text{ gcm}^{-3}$ ⁵⁾, $\rho_i = 2.25 \text{ gcm}^{-3}$ (from the density of SiC, 3.21 gcm^{-3} ⁵⁾, $\rho_i = \rho_{SiC}(m_{Si}/(m_{Si} + m_C))$, $\lambda_s = 23 \text{ \AA}$ ⁶⁾, and $\lambda_i = 15.6 \text{ \AA}$

⁴⁾, respectively. Fig.5 shows a plot of $R(\theta)$ as a function of $1/\sin\theta$ for various deposition times, based on the values given above. The fit to the linear function of Eq. (4) is shown in the figure. The 5 s deposition gave a slightly lower slope, indicating that the interface formation is not strictly completed at this point. The data points for deposition times greater than 10 s can be fitted well by a single line, and give a slope (d_i/λ_i) of 0.42 ± 0.02 so that d_i is 6.5 ± 0.3 Å, approximately 7 Å.

The interfacial carbide thickness of 7 Å determined above is significantly less than that suggested by Koidl and his coworkers³⁾. The accuracy of the thickness determined here depends of course on the accuracy of the numerical parameters assumed. The calculations also assume that the materials behave as a stack of ideal uniform slabs. However, it appears unlikely that the carbide thickness could be more than an order of magnitude greater than the obtained value, as suggested by Koidl and coworkers.

Unlike the hard a-C:H, a soft polymer-like film produced on the grounded electrode exhibits not only a low hardness (about 2 GPa)

but also poor adhesion, as judged by scratch adhesion tests. Thus the interface of the soft carbon film with the silicon substrate is expected to be considerably different from that of the hard a-C:H film. Fig.6 shows a typical Si 2p spectrum for the soft polymer-like film at a takeoff angle of 15°. The secondary peak maximum is located at about 101.8 eV, too high in energy to be attributed to silicon carbide. It resembles more a suboxide of silicon⁴). It should be noted that no such oxide peak was observed in the spectra of the control substrates which did not experience the plasma discharge. This suggests that the oxide layer was formed by the action of the plasma, possibly due to oxygen containing impurity species such as water related ions and radicals. As can be seen from Fig.6, taken near the grazing angle, the intensity of the oxide peak is extremely small. A similar calculation as used to determine the interfacial carbide thickness resulted in a submonolayer oxide thickness of roughly 1 Å.

The most important difference between the grounded and the powered electrode is the kinetic energy of impinging plasma ions. Under

our present deposition conditions, the incident ion kinetic energy exceeds 350 eV at the powered electrode, while it is approximately 15 eV at the grounded electrode²⁾. It seems reasonable to ascribe the interfacial carbide formation to high energy ion impact processes at the silicon substrate placed on the powered electrode. Theoretical calculations using TRIM code⁸⁾ result in a projected range or penetration depth for 350 eV C⁺ ions into a silicon target of 16 to 18 Å⁹⁾. Since the dominant ion impinging on the substrate is CH₃⁺²⁾, the actual range is expected to be comparable to our estimated thickness of the interfacial carbide of 7 Å. Thus, not only do the plasma ions act as structural modifier for a-C:H films, they are also likely responsible for the formation of an interfacial carbide and the resultant good adhesion to silicon substrates.

3.2 Sputter Depth Profile Studies

In addition to the XPS study presented above, we have done a series of SIMS depth profiling experiments hoping to extract the interfacial composition.⁹⁾ Both hard and soft a-C:H films more than 400 Å thick on silicon have been analyzed by using 5 kV argon ion sputtering. The

depth profiles as monitored with respect to Si_nC_m^+ ions manifested an ‘apparent’ interfacial silicon carbide phase both for the hard and for the soft carbon films. The thickness ranged from 100 to 150 Å in terms of FWHM of the interfacial peak in the depth profiles. The SIMS results are incompatible with the interfacial thickness determined in the XPS study. We believe that ion depth profiling methods lack the depth resolution necessary for the study of thin interfacial layer, due to ion-induced atomic mixing with the substrate.

4 CONCLUSION

Angle-resolved photoelectron spectroscopy has been used to investigate the interface of a-C:H films on silicon produced by plasma assisted chemical vapor deposition. The presence of approximately stoichiometric silicon carbide was demonstrated at the interface of hard a-C:H films produced under ion impact at the powered electrode. The effective thickness of the interfacial carbide was determined as approximately

7 Å. The interfacial carbide layer is likely responsible for the strong adhesion of the hard a-C:H films on silicon.

In contrast, no carbide layer was detected at the interface of soft polymer-like carbon films produced on silicon at the grounded electrode. The lack of the interfacial carbide could account for the poor adhesion of the polymer-like films on silicon.

The thickness of the interfacial carbide appears to correlate well with the average penetration depth of hydrocarbon ions in the plasma impinging on the substrate placed on the powered electrode. The plasma ions play a decisive role in the formation of the interfacial carbide and the resultant good adhesion to silicon substrate.

High energy sputter depth profiling methods introduce mixing of the exposed surface layers and often do not have the necessary depth resolution for the study of thin layers.

5 ACKNOWLEDGMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Research, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76F00098. Additional support of the work was provided by the ICI company. The authors would like to thank Greg Blackman and James Powers for helpful discussion.

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7 Figure Captions

1. Si 2p spectra for various deposition times on Si(100) placed on the powered electrode, where a hard a-C:H film is produced. (a) electron takeoff angle = 60° . (b) electron takeoff angle = 15° . The broken lines show the results of computer-assisted peak separation. The secondary peaks at higher binding energies are attributed to an interfacial silicon carbide layer.

2. C 1s spectra for various deposition times on Si(100) placed on the powered electrode, where a hard a-C:H film is produced. (a) electron takeoff angle = 60° . (b) electron takeoff angle = 15° . The broken lines show the results of computer-assisted peak separation. C 1s electrons from the carbide layer give rise to the lower binding energy component.

3. Relationship between the peak areas of Si 2p and C 1s signals associated with the interfacial silicon carbide layer. The data are collected for various deposition times (5 to ²⁰~~40~~ s) and electron takeoff angles (60° to 15°).

to 15°). The intensity ratio of near unity suggests the silicon carbide is approximately stoichiometric.

4. XPS spectra showing the O 1s, Si 2s, and Si 2p peaks at electron takeoff angles of 60° and 15° . Deposition time is 20 s on the powered electrode. The intensity is normalized to C 1s peak to account for the angle-dependent instrument factor. The lack of attenuation of the oxygen signal indicates that oxygen is not associated with the interface.

5. Dependence of $R(\theta)$ as defined in the text from the area intensity ratio of the chemically shifted Si 2p peak (from SiC) to the pure Si 2p peak (from Si substrate) on $1/\sin\theta$. θ represents the electron takeoff angle. Calculations using the slope of this plot yield a silicon carbide interfacial layer thickness of approximately 7 Å.

6. A Si 2p spectrum from a soft a-C:H film on silicon at electron takeoff angle of 15° . Deposition time is 20 s. A suboxide of silicon is present at the interface of these films at submonolayer levels.

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Fig. 1

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Fig. 2

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Fig. 3

Fig. 4

XBL-898 3045

Fig. 5

Fig. 6

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