Temperature effect on bonding structures of amorphous carbon containing more than 30at.% silicon

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Abstract

Bonding evolution of amorphous carbon incorporated with Si or a-C(Si) in a thermal process has not been studied. Unhydrogenated a-C(Si) films were deposited by magnetron sputtering to undergo two different thermal processes: i) sputter deposition at substrate temperatures from 100 to 500 °C; ii) room temperature deposition followed by annealing at 200 to 1000 °C. The hardness of the films deposited at high temperature exhibits a monotonic decrease whereas the films deposited at room temperature maintained their hardness until 600 °C. X-ray photoelectron spectroscopy and Raman spectroscopy were used to analyze the composition and bonding structures. It was established that the change in the mechanical property is closely related to the atomic bonding structures, their relative fractions and the evolution (conversion from C–C sp3 → C=C sp2 or C=C sp3 → C–Si sp3) as well as clustering of sp2 structures.

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1. Introduction

Unlike carbon atoms that will hybridize, silicon atoms can and only form σ bonds (sp3 configuration) with adjacent atoms. Because of this, silicon is considered a promising element to promote sp2-hybridized bonding in amorphous carbon (a-C). Silicon incorporation into amorphous carbon (a-C(Si)) causes the Raman G-peak of sp2 carbon pairs to downshift, accompanied by a decrease in the peak intensity ratio of disorder peak to graphitic peak (I_D/I_G) [1–4]. The decrease in I_D/I_G intensity ratio corresponds to the decrease in the average crystallite size of the sp2-bonded clusters [5], as well as the increase in sp3 fraction [6]. The disordering and loss of aromatic bonding cause the signature peak to downshift [5,7]. The addition of silicon also reduces the grown-in compressive stress [1,2,4], lowers friction coefficient and improve wear performance in humid atmosphere [8,9], and improves the blood compatibility of a-C [10,11].

Till date, numerous works have been conducted on silicon doping of a-C in atomic structures, in mechanical properties, and biological responses. However, the bonding evolution in a thermal process has not been looked into. A thermal process can modify atomic bondings, which in turn alters the properties of the films. Recent examples include the change in electrical properties [12] and the deterioration of blood compatibility [13] upon annealing. In this paper, we present the effect of thermal treatments on bonding structures and fractions of unhydrogenated a-C(Si) films deposited by magnetron sputtering. The change in hardness is then discussed in light of the atomic structures.

2. Experimental

2.1. Deposition of films

The basic sputtering deposition conditions were as follows: base pressure (4.5 × 10⁻³ Pa), process pressure (0.8 Pa), Ar flow rate (50 sccm) and substrate bias voltage (−10 V). Two sets of a-C(Si) films were deposited on silicon (100) wafer with the
graphite and silicon target power densities being 7.4 W/cm² and 2.5 W/cm² respectively: high temperature deposition (substrate temperature); and room-temperature deposition follow by annealing.

2.2. Annealing

The post-deposition annealing was conducted in a rapid thermal processor (Jipelec Jetfirst100) under Ar flow of 2000 sccm or Ar pressure of 1 atm at a ramping rate of 20 °C/s. After holding time of 3 min at temperature, the sample was cooled at around 6 °C/s.

2.3. Characterization

The atomic concentration and bonding configurations of Si and C were characterized by X-ray photoelectron spectroscopy (XPS, Kratos AXIS) using Al-Kα (1486.71 eV) at 15 kV under 10⁻⁶ Pa. The films were subjected to Ar ion etching for five minutes for surface cleaning prior to data collection. The broad C 1 s peaks are deconvoluted with Gauss-Lorentz distribution function after Shirley integrated background subtraction and the fitted curves had a reduced Chi-square of 1.2 or less to ensure convergence. The respective contribution of the various bonding configurations was calculated based on the deconvoluted peak area ratio. The bonding of a-C(Si) was also characterized by Raman spectroscopy (Renishaw Raman Spectroscope RM1000) with a HeNe laser wavelength of 633 nm at ~1 mW. The peak deconvolution was done using a Gauss-Lorentz distribution function, the fitted curves having a reduced Chi-square of 1.2 or less to ensure convergence.

The hardness of the films was determined using a Nanoindentor (MTS XP) equipped with a Berkovich diamond tip and continuous stiffness measurement capability. The indentation depth was set to ~10% of the coatings’ thickness (~300 nm) to avoid effect from the softer silicon substrate.

3. Results and discussion

Fig. 1 plots the hardness of the high temperature film together with the room temperature film as a function of processing temperature (deposition or annealing). Obviously the two different processes (deposition at high temperature or deposition at room temperature plus anneal at high temperature) give rise to vastly different mechanical responses: for high temperature deposition, the film hardness decreases with the increasing deposition temperature, while for the room temperature deposited film, the hardness maintains until 600 °C before falling when temperature increases further. A check on the composition of the films by XPS indicate that both sets of the a-C(Si) films have the same Si content of 36–38 at.%. So, what is happening? We explore the reasons from the following few...
aspects: $sp^2$ clustering, conversion from $sp^3$ to $sp^2$ and the activation energies of these processes.

3.1. $sp^2$ clustering

Fig. 2a shows Raman spectra of a-C(Si) thin films deposited at different substrate temperatures. The signature peak can be deconvoluted into graphitic (G) peak and disorder (D) peak respectively. The peak situated at 960 cm$^{-1}$ is from the bottom Si substrate. The G-peak is the signal from the $sp^2$ C bonding pairs in the a-C(Si) film; the D-peak arises due to breathing modes of the aromatic clusters. The intensity ratio of the two peaks ($I_D/I_G$) is presented in Fig. 3 as function of processing temperature. The formation and clustering of the $sp^2$ aromatic ring structures [5] increase the $I_D/I_G$ ratio. With increasing deposition temperature, the ordering increases (i.e., $I_D$ increases), the average size of $sp^2$-bonded clusters increases [5], at the same time, the $sp^3$ fraction reduces [6]. These combine and result in an increase in $I_D/I_G$ ratio. The up-shift of the signature peak of the amorphous carbon (c.f., Fig. 2a) comes from the ordering and formation of aromatic rings [5,7].

When the room temperature deposited-films are subjected to annealing, the signature peak location does not change below 600 °C (Fig. 2b). Above ~700 °C, however, the D-peak intensity increases sharply, as shown in the abrupt increase in $I_D/I_G$ ratio in Fig. 3. Graphitization (substantial increase in the $sp^2$-bonded clusters) causes up-shifting of the G-peak to around 1580 cm$^{-1}$ in response to removal of the disordering and increase in dominance of $sp^2$-crystallites. As Si is incorporated into the a-C, bonding of Si atoms to C prevents the nucleation of $sp^2$ clusters, which effectively retards the conversion of C–C $sp^3$ to C–C $sp^2$ configuration. That explains why as annealing temperature increases, there is no increase of $I_D/I_G$ until 600 °C. After ~600 °C, there is a rapid upshifting of the a-C(Si) G-peak position, an abrupt decrease in the G-peak linewidth and increase in $I_D/I_G$ ratio (Fig. 3). It is believed that at this temperature, the C $sp^3$ bondings start to breakdown, causing an instant increase in the number as well as the nucleation sites of $sp^2$ clusters. The 2nd order peak of Si substrate at ~960 cm$^{-1}$ (Fig. 2b) decreases as the annealing temperature goes beyond 600 °C. It shows the optical transparency of the a-C(Si) decreases, since the amount of the opaque C–C ($sp^3$) structures have increased. There are more ring structures as compare to olefinic (possess wider optical gap [5]). Band gap are found to decrease with increasing $sp^2$ contents [14–16]. On the other hand, pure a-C films whether hydrogenated or not have lower thermal stability during post annealing as graphitization begins at temperatures below 400 °C [17,18].

3.2. Bonding fractions

Fig. 4 is a typical deconvoluted C 1s core level spectra of a-C (Si). The C–C bonds at 284.3 eV belong to the $sp^2$ configuration. The $sp^3$ configuration, however, comes from either C–C bonds or C–Si bonds at 285.2 eV and 283.5 eV respectively. Taking the ratio of the area under the respective peaks over the whole C 1s peak as the percentage of each bonding configuration, one obtains Fig. 5. With increasing deposition temperature (Fig. 5a), the C–C $sp^3$ decreases drastically with the deposition temperature. This decrease indicates that the bulk of the C–C $sp^3$ bonds are being

Fig. 4. Deconvolution of C1 s peak of a-C(Si).

Fig. 5. The contribution of different bonding configurations from C 1 s peak of a-C (Si): a) deposited at different temperatures; b) annealed at different temperatures after deposition.
converted into C=C sp² and C–Si sp³ bonds (see trend of the other two curves in Fig. 5a). The thermal energy provided during the deposition process has given C–C sp³ metastable bonds enough energy to convert to a more stable C=C sp² bonding state. This also promotes the bonding between C and Si atoms therefore an increase in the C–Si sp³ bonding configuration is seen.

Fig. 5b plots the bonding fraction of the “room temperature film” after annealing. The C–Si sp³ bonds increase from 200 to 600 °C, and then maintain their level all the way to 1000 °C. Meanwhile, C–C sp³ and C=C sp² fractions decrease slightly till 600 °C. Above 600 °C, a drastic increase in C=C sp² fraction and an abrupt decrease in C–C sp³ are experienced. The decrease in C–C sp³ means the conversion of sp³ → sp² takes place (that is why there is an increase in C=C bonding). This conversion, however, seems to take place at a temperature as low as ~ 200 °C, though slowly. Above 600 °C, an avalanche of the conversion takes place, giving rise to the sharp increase of \( I_D/I_G \) (Fig. 3) and a drastic softening of the film (Fig. 1). During 200 to 600 °C, C=C sp² bonding decreases; this corresponds to an increase in C–Si sp³ bonds. It is conjectured that the broken-up C atoms bond with free or under-coordinated Si to form C–Si bonds, giving rise to an increase in C–Si sp³ fraction. At 600 °C, the “free” Si is used up, therefore, further increase of temperature witnesses direct conversion of C–C sp³ to C=C sp² (one drops and the other hikes) while C–Si fraction maintains constant.

3.3. Activation

The conversion process can be better understood through an examination of the activation energies of the process involved. Both sp³ → sp² conversion and sp² site clustering are main reasons for the degradation of the mechanical properties. Since the sp³ → sp² conversion process is a process of atomic bond breaking and reformation, the process is rate-limited by the atomic jumping frequency and temperature. For such a process, the activation energies can be estimated by \( k\ln(\nu) \) where \( k \) is Boltzmann constant, \( T \) is temperature in Kelvin, \( \nu \) is atomic jumping frequency, and \( \tau \) is the time taken to realize the transition. Typically, \( \nu \sim 1 \times 10^{14} \) Hz. For high temperature deposition, \( I_D/I_G \) (Fig. 3) or C=C(C(Fig. 5a) already increased at 100 °C. For sake of convenience, take this as the transition temperature for estimation. For the room temperature films, take 600 °C annealing as the transition temperature, and for simplicity, \( \tau \sim 1 \) s, the activation energies for the sp³ → sp² conversion are estimated as ~1.1 eV for high temperature deposition and ~2.4 eV for post deposition annealing, more than 2 times that of high temperature deposition. The activation energies of sp² clustering can be extracted from the Arrhenius plots of \( I_D/I_G \) ratio (ln\([I_D/I_G] \) vs 1/T): ~0.07 eV (Fig. 6a) for high temperature deposition, and ~0.34 eV for post deposition annealing (Fig. 6b), 5 times higher than that in high temperature deposition. Obviously, both transition from sp³ to sp² and clustering of sp² are much easier at high temperature deposition where disordering is hard to maintain due to the dynamic annealing effect.

4. Summary

The drop in hardness of the a-C(Si) film comes from two aspects: (1) the transition of sp³ to sp², (2) the clustering of the sp² structure. When the thermal processing is done in situ, the activation energies for both processes are much less than that for post deposition annealing. That accounts for the holding of hardness till 600 °C in the case of room temperature deposition plus post annealing. Because of the low activation energy, for high temperature deposition, Si atoms doped are not able to prevent the nucleation of sp² clusters nor can they prevent the conversion of bonds in sp³-configuration to sp². During energetic bombardment, the energy possessed by an impinging particle is converted into thermal energy at a point [19] or along a line (trajectory) [20], the energy then disperses outwards by thermal diffusion. When the deposition takes place at high temperature, this thermal relaxation takes place effectively (because of the atomic mobility) and atoms rearrange themselves into a more stable state and bonding configuration (i.e., formation of C=C sp²-hybridized bonds). In the case of room temperature deposition, however, atomic mobility is low, the thermal energy from the impinging particles gets dissipated away quickly (because of the thermal gradient) and the ions then get quenched-in (trapped in) the structure, giving rise to higher possibility of forming more C–C sp³-hybridized bonds.

5. Conclusions

The a-C(Si) films deposited at 100 to 500 °C experience deteriorating hardness with deposition temperature. The same
films deposited at room temperature and then subjected to annealing at the same temperatures maintain the room temperature hardness to 600 °C. The hardness decrease is attributed to sp³ to sp² conversion and clustering of sp² structures. Comparing room temperature deposition plus annealing with high temperature deposition, the activation energies is twice as high for sp³ to sp² conversion, and 5 times for sp² clustering. Si in a-C retards the conversion from sp³ to sp² bonding during annealing through formation of C–Si sp³ bonds.

References