Structure and properties of Si incorporated tetrahedral amorphous carbon films prepared by hybrid filtered vacuum arc process

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Abstract

The mechanical properties and atomic bond structure of Si incorporated into tetrahedral amorphous carbon (ta-C) films were investigated. The films were deposited by a filtered vacuum arc of graphite with simultaneous sputtering of Si. The Si concentration in the film could be controlled by changing the flow rate of the Ar sputtering gas. It was observed that the incorporated Si preferentially substituted sp bonded carbon when the Si concentration was less than 2.5 at.%. Since the Si–C bond generated by substitution was weaker than C–C bond, the Si incorporation could cause the relaxation of nearby distorted C–C bonds by inducing large strain in the Si–C bond. This structural change resulted in a significant decrease in the residual compressive stress in this Si concentration range. In contrast, the incorporated Si which has only sp$^3$ hybridization, generated the weaker Si–C bonds without breaking the three-dimensional interlinks of the atomic bond structure. Hence, the hardness and the plane strain modulus gradually decreased with Si incorporation. The saturated mechanical properties observed when the Si concentration was higher than approximately 10 at.% are due to the formation of a large amount of SiC phase in the deposited film.

Keywords: Tetrahedral amorphous carbon; Si incorporation; Filtered vacuum arc; Reduction of residual stress

1. Introduction

Tetrahedral amorphous carbon (ta-C) films can be deposited by bombarding a high flux of carbon ions of kinetic energy ranging from 10 to 100 eV onto the deposited surface. Various thin film processes using mass selected ion beams [1], pulsed laser ablation [2] or filtered vacuum arcs [3] could provide the required deposition conditions for high quality ta-C film synthesis. Owing to high hardness up to 80 GPa, high optical transparency, excellent tribological properties and a high ratio of sp$^3$ hybridized carbon bonds, ta-C films have drawn much attention in both scientific and engineering aspects. However, high residual compressive stress, presumably due to the high flux ion bombardment, results in poor adhesion of the film, which significantly limits their applications. The high residual stress also causes ambiguities in the characterization of the ta-C film using Raman spectroscopy [4] or nanoindentation [5]. Many attempts have been thus reported to reduce the stress of ta-C films; i.e. substrate biasing [6], annealing after deposition [7] or boron incorporation [8].

Si has been considered as an important alloying element to modify the structure and properties of hydrogenated amorphous carbon (a-C:H) films. Si incorporation into a-C:H films was reported to improve the adhesion [9], thermal stability [10] or tribological properties in a humid environment [11]. The effects of the Si incorporation on the mechanical properties appeared to depend on the deposition conditions [12,13]. Details of the structural changes in a-C:H films deposited by rf-PACVD using mixtures of benzene and silane were recently reported by the present author [12]. Si addition to ta-C films would, thus, be effective in controlling the structure and its physical and chemical properties. In addition, due to the lack of hydrogen, the relationship between the atomic bond structure and the mechanical...
Properties can be more readily addressed in ta-C films. Recently, the Si addition effect on the residual stress and the mechanical properties of ta-C film was reported by Shi et al. in the range of Si concentration from 2.4 to 48 at.% [14]. They showed that the residual stress was reduced from 8.0 to 2.1 GPa by Si addition, which was accompanied by a hardness reduction from 60 to 22 GPa. However, the effect of a small amount of Si addition on the structure and properties of ta-C films has not yet been reported.

In the present work, Si was added to ta-C films by using a filtered vacuum arc of graphite combined with d.c. magnetron sputtering of crystalline Si. The Si concentration in the film could be controlled in a systematic way by changing the flow rate of the Ar sputtering gas. We observed that a small amount of Si incorporation (<1 at.%) significantly reduced the residual compressive stress of the film, whereas the decrease in hardness and elastic modulus was not as significant as that in the residual stress. Analysis of the atomic bond structure showed that the behavior of the mechanical properties with Si concentration is intimately related with the C–Si bonds in the deposited film.

2. Experimental

Fig. 1 shows the schematic of the hybrid-type filtered vacuum arc deposition system used in the present work. The arc plasma generated at the graphite cathode was introduced to the reaction chamber after magnetic filtering of macro particles. A magnetron sputtering source of Si was installed in the reaction chamber at approximately 45° from the arc plasma beam. A water-cooled substrate holder was placed normal to the arc plasma beam at a distance of 30 cm from the exit of the FVA source. Ar sputtering gas was supplied via gas feed-through placed near the sputter gun. The flow rate of Ar was controlled by a mass flow controller to change the Si concentration in the deposited films. The base pressure of the vacuum system was less $10^{-4}$ Pa. The film was deposited at a pressure of $10^{-2}$ Pa using both a carbon arc plasma beam and sputtered Si atoms. Because of the high electron flux in the vacuum arc plasma, the sputtering of Si could be simultaneously performed at the deposition pressure. A Si (100) wafer of thickness 510 μm was used for the substrate. The growth rate of the film decreased with the Ar flow rate and showed a minimum when the Ar flow rate was approximately 13 sccm. However, the growth rate of the film increased again when the Ar flow rate was beyond 13 sccm. The film thickness was fixed at 100 nm in all specimens by changing the deposition time. Prior to deposition, the substrate was pre-cleaned by using the carbon arc plasma beam mixed with Ar ions at a negative bias voltage of −800 V. During deposition, the substrate was grounded to minimize the Ar sputtering of the film. A thin Si (100) strip of thickness 100 ± 5 μm was also used to measure the residual stress of the film. The residual stress was obtained from the curvature of the film/substrate composite using Stoney’s equation [15]. The composition of the deposited film was measured by Rutherford back scattering spectrometry (RBS) using a collimated 4He$^+$ ion beam of 2 MeV. Nanoindentation in continuous stiffness mode was employed to characterize the hardness and the plane strain modulus of the film [16]. The atomic bond structure was analyzed by using Raman spectroscopy and Fourier transform infra-red spectroscopy (FTIR). Raman spectra were obtained by a triple-Raman spectroscope in the range from 800 to 2000 cm$^{-1}$, using an Ar ion laser of 514.5 nm wavelength to induce Raman activation. FTIR spectra were obtained in a vacuum at room temperature using normal incident conditions.

3. Results and discussion

In the present hybrid deposition system, the Si concentration of the film could be controlled in a systematic way by changing the flow rate of the Ar sputtering gas. Fig. 2 shows the composition of the deposited film for various Ar flow rates. When the Ar flow rate was less than 9 sccm, we could not obtain the Si incorporated ta-C film due to unstable ignition of the magnetron sputter source. However, as the Ar flow rate increased from 9 to 12 sccm, the Si concentration in the film increased from 0.5 to 2.5 at.%. When the Ar flow rate was higher than 12 sccm, a significant increase in Si concentration was observed with increasing Ar flow rate. When the Ar flow rate was 18 sccm, the Si concentration of the film was 85.0 at.%. In all samples, a small amount of oxygen was also incorporated with Si, which seems to be due to the surface oxide layer of the Si sputter target or residual water molecules in the deposition chamber. Although pre-sputtering of the target before the film deposition could reduce the oxygen.

Fig. 1. Schematic of hybrid filtered vacuum arc system used in the present work.
incorporation in the film, oxygen of a maximum of approximately 5 at.% was still observed when the Si concentration was higher than 30 at.%. However, the ratio of oxygen to silicon was less than 0.1 in most cases. The effect of oxygen on the structure of the film was assumed to be negligible in the present work.

The Si incorporation significantly reduced the residual compressive stress of the deposited films. As shown in Fig. 3, the residual stress sharply decreased from 6.0 to 3.3 GPa by adding 1 at.% of Si to the ta-C films. Beyond 1 at.% of Si, the residual stress gradually decreased to 0.8 GPa as the Si concentration increased to 50 at.%. It must be noted that most of the reduction of the residual compressive stress was observed when a small amount of Si was incorporated: 52% of the total reduction occurs when the Si concentration was less than 1 at.%. Hardness and the plane strain modulus of the deposited film are summarized in Fig. 4. In contrast to the residual compressive stress, the mechanical properties gradually decreased with increasing Si concentration. In the range of the Si concentration from 0 to 8.5 at.%, the hardness was reduced from 40.7 to 21.7 GPa, and the plane strain modulus from 354 to 200 GPa. Further increasing the Si concentration resulted in saturated values of the hardness and the plane strain modulus, which are comparable to those of nanocrystalline SiC (20 GPa in hardness and 220 GPa in plane strain modulus) [17]. (Because the film thickness is approx. 100 nm, the uncertainties due to the substrate effect should be considered in the nanoindentation measurements [18]. The substrate effect will cause underestimation of film hardness in the present system of hard films deposited on soft substrate. On the other hand, a high level of the residual compressive stress also induces the uncertainty in the hardness measurement [5]. The hardness will be over-estimated by the residual compressive stress due to the pile-up of materials near the indenter. Both effects are more significant in films of higher hardness and residual compressive stress. It was, thus, assumed that the net effect of the uncertainties is negligibly small.)

Fig. 5a shows the Raman spectra obtained from the Si incorporated ta-C films. The numbers on the spectra were the Si concentrations in at.%. Because of higher sp$^3$ fraction in the ta-C film which reduces the sensitivity to the Raman activation, the intensity of the carbon Raman peak in ta-C film is generally smaller than that of the hydrogenated amorphous carbon film. Further-
more, the D peak shoulder is much weaker in ta-C films, resulting in a more symmetric carbon Raman peak of single broad feature centered at approximately 1560 cm\(^{-1}\). The broad peak at approximately 960 cm\(^{-1}\) is second-order peak of the Si substrate, of which intensity is, thus, proportional to the optical transparency of the film. The Raman spectra of amorphous carbon films can be resolved by two Gaussian peaks which are, respectively, associated with D and G peaks of solid carbon materials [19]. Because of the symmetric shape of the carbon Raman peak, the spectrum was deconvoluted into a broad D peak and a sharp G peak. The broad D peak seems to represent a higher degree of disorder in sp\(^2\) domain boundaries. Consequently, there were relatively large errors in determining the ratio \(I_D/I_G\), the D peak position, and the full width at half maximum (FWHM) of each peak. However, the error in the G peak position is sufficiently small to allow structural changes of the films to be reflected. The error in the G peak position, estimated to be \(\pm 1.5\) cm\(^{-1}\), is mainly due to uncertainty in the baseline correction. Fig. 5b shows the fitting results of the G peak position for various Si concentrations (solid circle). Recently, Shin et al. showed that the residual compressive stress shifted the G-peak to higher wavenumber by 4.1 cm\(^{-1}\)/GPa [4]. Data represented by open circles in Fig. 5b are the corrected G peak positions where the residual stress effect was excluded by using the stress data of Fig. 3. Hence, the data of open circles reflect only the structural change due to the Si incorporation. It was empirically known that a higher content of sp\(^3\) bonds resulted in a shift of the G peak to a higher wave number in both ta-C and hydrogenated amorphous carbon films, if one can exclude the effect of the residual stress [4].

When the Si concentrations were lower than 2.5 at.\%, the shape and the intensity of the Raman spectra were essentially the same as those of pure ta-C films (Fig. 5a). Furthermore, as can be seen in Fig. 5b, the G peak position did not vary significantly with Si incorporation in this Si concentration range. These results show that the ratio of sp\(^3\)/sp\(^2\) in the film was kept almost constant when the concentration of incorporated Si was lower than 2.5 at.\%, which implies that the Si atoms preferentially substituted the carbon atoms of sp\(^3\) bonds. The structural information obtained from the Raman spectrum analysis can explain the observations of Figs. 3 and 4 that the residual stress of the film was significantly relaxed by adding a small amount of Si, while the hardness gradually decreased with Si concentration. When the Si concentration of the film was low, one can expect that most Si atoms which substitute the carbon atoms of sp\(^3\) bonds would be isolated from each other. Since the strength of Si–C bonds (3.21 eV) is smaller than that of sp\(^3\) C–C bonds (3.70 eV) [20], the Si-incorporated site can play a role in compensating for the distortion of the nearby sp\(^3\) C–C bonds. Relaxation of the residual stress would occur with large strains in the Si–C bonds. The effect would be most significant when a small amount of Si was added to pure ta-C films of high residual stress. On the other hand, the hardness of the film is proportional to the degree of three-dimensional interlinks of the atomic bond structure which would be enhanced by the sp\(^3\) bond [21]. Because the incorporated Si atom substitutes the carbon of the sp\(^3\) bond, the degree of three-dimensional interlinks would not be reduced by the incorporated Si atoms, which have only sp\(^3\) hybridization bonds. The decrease in the hardness is, thus, due to the weaker Si–C bonds rather than the decrease in the three-dimensional interlinks, resulting in a gradual change of the hardness in this concentration range.

When the Si concentration was higher than 2.5 at.\%, the shape of Raman spectra becomes different from
those of pure ta-C films. Increasing Si concentrations resulted in higher intensity of the G peak with the center at lower wavenumber. The intensity of the second order Si peak at 960 cm\(^{-1}\) also decreased. As can be judged from the G peak position data of Fig. 5b, the fraction of sp\(^3\) hybridized carbon bond increases in this concentration range. This spectral change shows that the incorporated Si substituted the carbon atoms in sp\(^2\) clusters, which would reduce the content of carbon atoms sensitive to the Raman activation. However, it must be noted that the increase in the sp\(^3\) fraction is mainly due to the increased fraction of Si–C bonds. The symmetry breaking of the aromatic sp\(^2\) clusters due to the Si substitution would result in higher intensity of the G peak [22]. Furthermore, the Raman peak at approximately 1450 cm\(^{-1}\) which is associated with SiC phase can affect the intensity and the position of the G peak [17]. The decrease in optical transparency observed in this concentration range is also due to the increased content of Si–C bonds. It can, thus, be said that the increase in the content of SiC phase is the dominant structural change in the Si concentration range from 2.5 to 22 at.%. The formation of an SiC phase at a higher Si concentration was also confirmed by the FTIR spectra shown in Fig. 6. While the spectra did not vary until the Si concentration was 4 at.%, a significant SiC stretching absorption band centered at 750 cm\(^{-1}\) started to appear when the Si concentration was 8.5 at.% [23]. The saturated behavior of the mechanical properties whose values are comparable to those of SiC is, thus, a consequence of the large amount of SiC phase formation in the deposited film. When the Si concentration is higher than 22 at.%, the intensity of the Raman peak decreased and eventually disappeared at the Si concentration of approximately 50 at.% due to the profound effect of reduction of carbon concentration.

4. Conclusions

The composition of the Si-incorporated ta-C films could be controlled by changing the flow rate of Ar sputtering gas in the hybrid filtered vacuum arc process. The mechanical properties and the atomic bond structure of the Si incorporated ta-C films were investigated over a wide range of Si concentrations. The most important result of the present work is that a small amount of Si addition to ta-C films could significantly reduce the residual stress with a little degradation of the mechanical properties. When the Si concentration was higher than 10 at.%, the residual stress and the mechanical properties were saturated to the values of SiC phase. The observed behavior could be understood in terms of the changes in the atomic bond structure caused by the Si incorporation. The first apparent effect of the Si incorporation was to substitute the sp\(^3\) carbon atoms, generating weaker Si–C bonds. The large strain of the weaker Si–C bonds caused the relaxation of distorted C–C bonds near the Si. However, this change in atomic bond structure did not change the fraction of sp\(^3\) bonds in the film. Therefore, the hardness and the elastic modulus which are intimately related with the three-dimensional interlinks gradually decreased with Si concentration. Further increasing the Si concentration generated the SiC phases, resulting in the saturated mechanical properties comparable to those of SiC.

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References