



Structure and mechanical properties of Ag-incorporated DLC films prepared by a hybrid ion beam deposition system

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Abstract

Ag-incorporated diamond-like carbon films were prepared on Si(100) wafers using a hybrid deposition system composed of an end-Hall-type hydrocarbon ion gun and a silver DC magnetron sputter source. The Ag concentration in the films was controlled by changing the fraction of Ar in the Ar and benzene reaction gas. The chemical composition, microstructure, atomic bond structure, and mechanical properties were investigated for Ag concentrations ranging from 0 to 9.7 at.%. When the Ag concentration was 0.1 at.%, the Ag atoms were fully dissolved in the amorphous carbon matrix without forming any second phase. Amorphous and crystalline silver particles appeared when the Ag concentration was 1.7 and >6.8 at.%, respectively. It was found that the hardness was not sensitive to the Ag concentration in this concentration range. On the other hand, the residual compressive stress was strongly dependent on the chemical state of the incorporated Ag atoms. The mechanical properties are discussed in terms of the changes in the microstructure and atomic bond structure induced by Ag incorporation.

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1. Introduction

Diamond-like Carbon (DLC) films have been widely studied owing to their excellent mechanical properties, chemical inertness and bio-compatibility [1–4]. However, high residual compressive stresses and low adhesion are the main drawbacks for many practical applications [5–7]. To reduce the residual stress and to enhance the adhesion and tribological properties of the DLC films, incorporation of transition metals which form carbides, such as Ti, Mo, Cr, W, has been extensively investigated [8–11]. Despite research on the effects on film stress following the incorporation of transition metals into DLC films, no studies have been performed on the effect of the incorporation of noble metals on the structure and the mechanical properties of the DLC films to our knowledge. For Ag-incorporated DLC films, studies have been reported on the electrochemical, biological, and tribological properties [12–15].

Our recent first-principles calculations reported the total energy of a system with changes in the bond angles between the metal (Ti, Mo, Cr, W, Ag, Au, Al, Si, etc) and carbon atoms in order to understand the effect of metal atoms in an amorphous carbon network on the residual compressive stress [16]. In a pure carbon system, the total energy increased substantially as the bond angle deviated from the equilibrium angle of the tetrahedral sp^3 bonds, which would be the reason for the high residual compressive stress of amorphous carbon films. However, the increase in the total energy was significantly reduced by the addition of noble metals as well as transition metals. It was suggested that both noble metals and transition metals dispersed in the amorphous carbon matrix may play the role of a pivotal site, resulting in the reduction of the residual stress in the amorphous carbon network from distortion of the bond angle. Note that stress reduction of Ag-incorporated DLC films is also essential for biological applications in order to exhibit good anticorrosion and antimicrobial properties.

In this work, we investigated the effect of Ag incorporation on the mechanical properties of DLC films. This study was the first attempt to deposit Ag-incorporated DLC films using a

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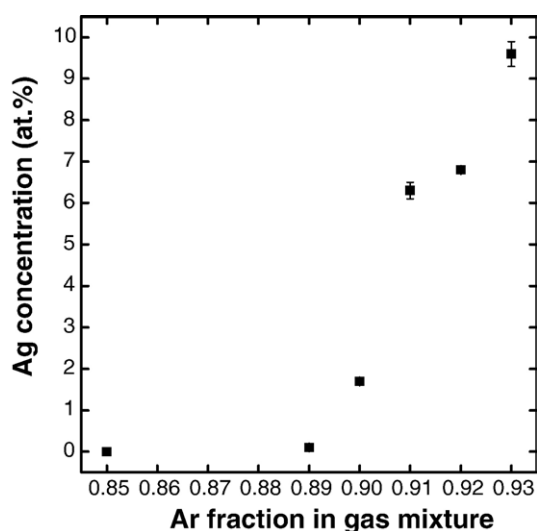


Fig. 1. Dependence of Ag concentration in the film on the fraction of Ar in the reaction gas.

hybrid deposition method composed of a hydrocarbon ion beam and a DC magnetron sputtering of Ag. We focused on the relationship between the mechanical properties and the structure of the films caused by the incorporation of Ag. It was observed that the residual compressive stress was strongly dependent on the concentration and the state of Ag atoms, whereas the hardness was not sensitive to the concentration of Ag.

2. Experimental

Ag-incorporated DLC films were deposited on a *p*-type Si(100) wafer by using a hybrid ion beam deposition system. The hybrid system is composed of ion beam deposition of benzene and DC magnetron sputtering of high purity (99.99%) silver as shown elsewhere [11]. The benzene was introduced into an end-Hall-type ion gun to obtain hydrocarbon ions and the Ag target was sputtered by Argon. Prior to deposition, the chamber was evacuated down to 2×10^{-5} Pa, then the Si wafer was cleaned using an Ar ion beam employing a pressure of 0.10 Pa and a bias voltage of -400 V for 30 min. A buffer layer of DLC film of 52 ± 3 nm thickness was deposited at a bias voltage of -800 V. This pretreatment is essential in order to obtain stable incorporation of Ag into DLC films. Subsequently, a Ag-incorporated DLC film with 150 ± 20 nm thickness was deposited. All the Ag-incorporated DLC layers were deposited using a substrate bias voltage of -200 V whereas the deposition pressure varied in the range from 0.08 to 0.15 Pa, depending on the fraction of Ar in the reaction gas. Pure DLC films were also prepared using the hydrocarbon ion beam without operating the sputter gun. The fraction of Ar in the reaction gas varied from 0.85 to 0.93 to control the Ag concentration in the deposited films.

The thickness of the films was measured by using an α -step profilometer employing a step made by a shadow mask. The residual stress of the film was measured from the curvature of the film deposited on a thin Si(100) strips of thickness 100 ± 2 μ m and calculated using the Stoney equation [17]. Nanoindentation in continuous stiffness measurement (CSM) mode was used to

characterize the hardness using a Berkovich diamond tip. The composition of the film was analyzed using Rutherford backscattering spectrometry (RBS) employing a 2 MeV collimated $^4\text{He}^{2+}$ ion beam. 2 MV Pelletron accelerator was used for the acceleration of He ion and a home-made analysis chamber was used to collect the RBS spectra. Micro-Raman spectroscopy using Ar ion laser having a wavelength of 514.5 nm was also used to characterize the atomic bond structure of the films. High resolution transmission electron microscopy (HRTEM) was employed to characterize the microstructure. Cross-sectional TEM samples were prepared using focused ion beam (FIB) to minimize any thermal effects on the microstructure.

3. Results and discussion

Fig. 1 shows the dependence of the Ag concentration in the films on the fraction of Ar in the reaction gas. When the Ar fraction was less than 0.85, the incorporation of Ag in the DLC films was not detected, probably due to a substantial poisoning of the Ag target caused by the high flux of hydrocarbon ions. However, as the Ar fraction increased from 0.89 to 0.93, the Ag concentration in the film increased monotonically from 0.1 to 9.7 at.%. These results show that the Ag concentration in the film can be systematically controlled by varying the fraction of Ar in the reaction gas. This observation is consistent with our previous results on the W-incorporated DLC films [11].

Fig. 2 shows the effects of the Ag concentration in DLC films on the residual compressive stress and hardness. A slight reduction of the residual compressive stress by the incorporation of 0.1 at.% Ag was followed by the significant decrease from 2.9 to 1.6 GPa by varying the Ag concentration from 0.1 to 1.7 at.%. Further incorporation of Ag up to 9.7 at.% induced a gradual decrease of the residual stress down to 1.3 GPa. The incorporation of Ag also resulted in the reduction of the hardness from 22.6 ± 0.5 to 16.9 ± 0.2 GPa. However, the change in the hardness was not as significant as that seen in the residual

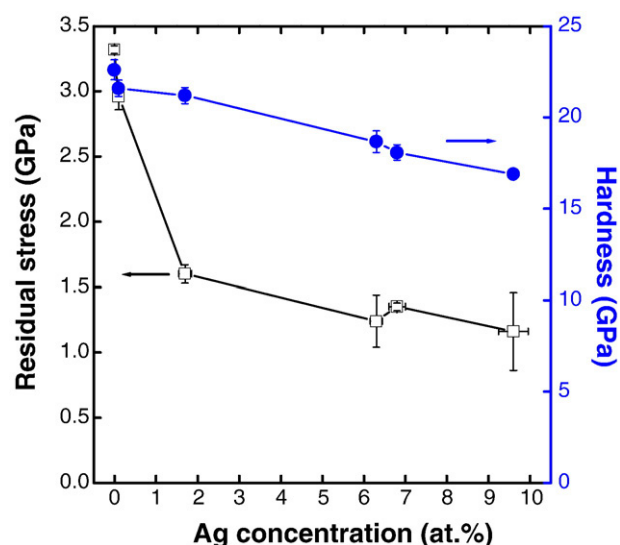


Fig. 2. Residual compressive stress and hardness of Ag-incorporated DLC films as a function of Ag concentration.

stress. Note that the DLC films with 1.7 at.% Ag incorporation showed a significant reduction in the residual stress without a considerable degradation of the hardness, implying that DLC films with low concentration of Ag is effective from the perspective of mechanical properties. Further incorporation of Ag induced a gradual reduction of hardness concurrent with a

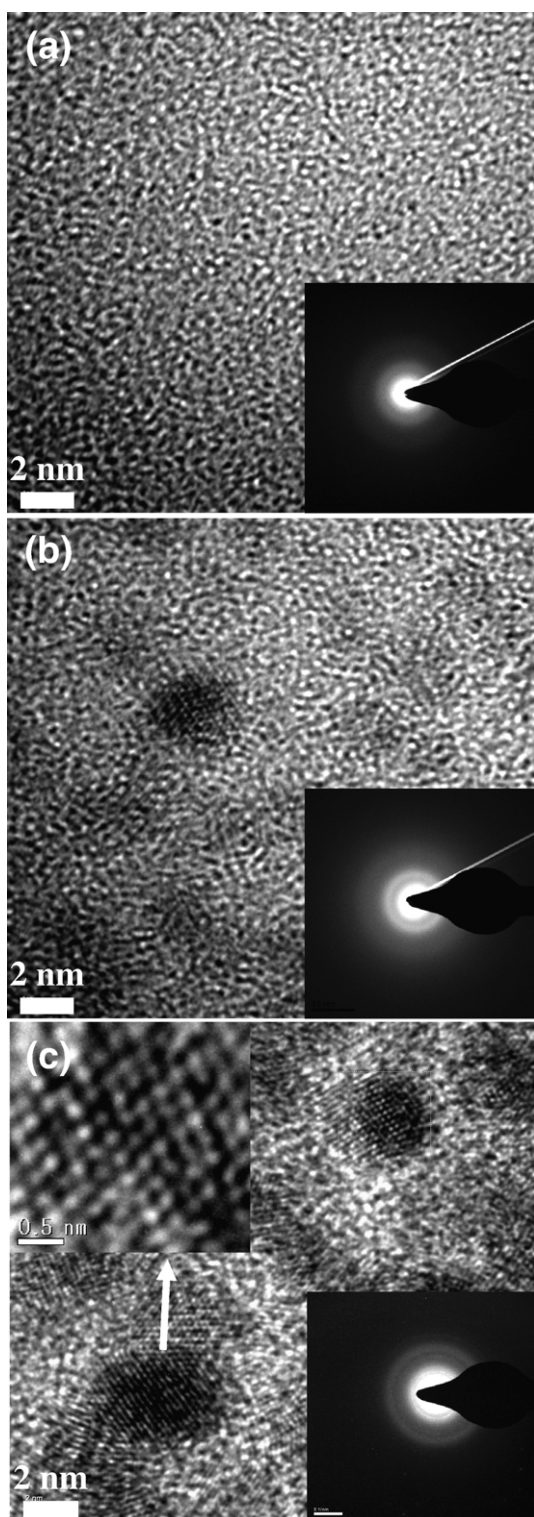


Fig. 3. HRTEM images of DLC films with Ag concentration of (a) 0.1 at.%, (b) 1.7 at.%, and (c) 9.7 at.%. Each inset shows the SAD pattern of the corresponding image.

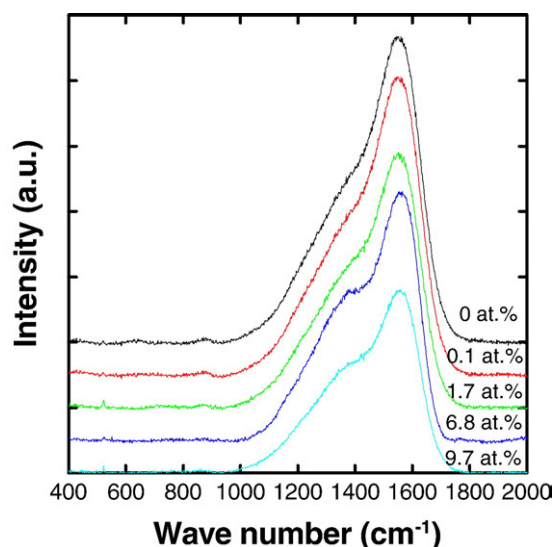


Fig. 4. Micro-Raman spectra of DLC films with various Ag concentrations. The spectra were normalized with respect to the film thickness.

similar reduction of the residual stress. Since the films are not thick enough to exclude the substrate effect on the hardness, the uncertainties caused by the substrate should be considered in the nanoindentation measurements. The softer Si substrate may induce an underestimation of the hardness of the harder DLC films. On the other hand, the residual compressive stress may cause an overestimation in the hardness measurements due to the pile-up of materials near the indenter [18,19]. Thus, the net uncertainties in hardness are expected to be negligible.

Fig. 3 shows HRTEM microstructures and selected area diffraction (SAD) patterns of DLC films with various Ag concentrations. At the Ag concentration of 0.1 at.%, a uniform amorphous structure was observed as shown in Fig. 3a. This microstructure is essentially the same as that of pure DLC films, indicating that all the incorporated Ag atoms were fully dissolved in the amorphous carbon matrix. However, when the concentration of incorporated Ag was 1.7 at.%, the Ag atoms began to segregate and form an amorphous silver phase with a diameter of approximately 2 nm and disperse in the carbon matrix as shown in Fig. 3b. The darker spots correspond to metallic Ag region, while the brighter region corresponds to the DLC matrix, respectively. Upon further incorporation of Ag to 9.7 at.% (Fig. 3a), Ag crystallines of FCC phase with a size

Table 1
Micro-Raman spectra for DLC films with various Ag concentrations

Ag concentration (at.%)	$I(D)/I(G)$	FWHM of G peak (cm ⁻¹)	Position of G peak (stressed) (cm ⁻¹)	Position of G peak (unstressed) ^a (cm ⁻¹)
0	0.71	66.8	1562	1550
0.1	0.71	66.7	1562	1550
1.7	0.78	64.9	1562	1556
6.8	0.87	57.3	1568	1563
9.7	0.86	57.2	1567	1562

^a Corrected position of the G peak from the position of G peak (stressed) by excluding the residual stress effect [20] using the stress data in Fig. 2.

ranging from 4 to 6 nm were observed, which were revealed by the lattice fringes and the ring patterns in the inset of Fig. 3c. The first and second ring patterns correspond to the (111) and (200) of FCC silver phase, respectively.

Fig. 4 shows the Raman spectra obtained from the Ag-incorporated DLC films, which are vertically shifted for ease of comparison. The spectra were deconvoluted into *D* and *G* peaks, respectively using two Gaussian curves. Table 1 summarizes the characteristics of the Raman spectra of DLC films with various Ag concentration. The incorporation of 0.1 at.% of Ag did not induce any change in the atomic bond structure. On the contrary, further incorporation of Ag resulted in the increase of the intensity ratio of *D* peak and *G* peak, $I(D)/I(G)$ and the narrowing of the *G* peak. In addition, the position of *G* peak shifted over a considerable range from 1550 to 1562 cm^{-1} when the Ag concentration increased from 0.1 to 9.7 at.%. These characteristics obviously imply the increase of the graphite-like bonds in amorphous carbon matrix [21].

Considering the mechanical properties and the structural analyses, the decrease in the residual stress induced by the 0.1 at.% Ag incorporation is concurrent with the uniform dissolution of Ag in the carbon matrix without any structural change of the matrix. This may be explained by our recent first-principles calculations, suggesting that Ag atoms in the amorphous carbon matrix play the role of a pivotal site due to the decrease in both the strength and directionality of the bonds while keeping the three-dimensional bond network [16]. When 1.7 at.% of Ag is incorporated into DLC films, a considerable decrease in the residual stress occurred presumably due to the formation of a metallic amorphous phase acting as efficient buffer sites to absorb the stress in the carbon matrix. On the contrary, a slight increase in the sp^2/sp^3 ratio induced a minor decrease in the hardness in this composition. These results can be understood if one considers that each metallic particle is isolated in the amorphous carbon matrix. Further incorporation of Ag up to 9.7 at.% decreased the residual stress gradually down to 1.3 GPa, which correlates with the evolution of the crystalline Ag phase as well as the increase in the sp^2/sp^3 ratio. Such a gradual decrease in the residual stress at higher Ag concentrations can be considered as an analogy of the percolation structural transition of a transition metal incorporated a-C:H structure [11,22,23]. These results show that an optimal concentration of Ag in DLC films is required for the formation of well-dispersed metallic phase while keeping the three-dimensional interlink of the amorphous carbon network, which would result in a significant reduction in the residual stress without a considerable degradation of the hardness.

4. Conclusions

A hybrid ion beam deposition system composed of an end-Hall-type ion gun and DC magnetron sputtering has been successfully employed to deposit Ag-incorporated DLC films. The Ag concentration of the films could be varied from 0 to 9.7 at.% by changing the fraction of Ar gas in the mixture of Ar and benzene. When the Ag concentration was 0.1 at.%, the Ag atoms were fully dissolved in the amorphous carbon matrix. The Ag atoms are suggested to play a pivotal role due to the weak bond between C and Ag atoms, resulting in the reduction of the residual

stress. However, the mechanical properties of the film did not show a significant decrease since the three-dimensional interlink of the atomic bond network in the carbon matrix remained nearly unchanged in this composition. Amorphous and crystalline Ag particles were observed when the Ag concentration was 1.7 and >6.8 at.%, respectively. In this composition range, the metallic nanoparticles are supposed to act as efficient buffer sites to absorb the residual stress in the carbon matrix, inducing a noticeable decrease in the residual stress. However, a slight increase in the sp^2/sp^3 ratio results in a minor decrease in the hardness. This work shows the possibility of fabricating the Ag-incorporated DLC films with a reduced residual stress, without any considerable degradation of the hardness, indicating that these films have a potential for use in biological applications.

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