

Unusual stress behavior in W-incorporated hydrogenated amorphous carbon films

Ai-Ying Wang,^{a)} Hyo-Shin Ahn,^{a)} Kwang-Ryeol Lee,^{b)} and Jae-Pyoung Ahn^{c)}
*Future Technology Research Division, Korea Institute of Science and Technology, P.O. Box 131,
 Cheongryang, Seoul 130-650, Korea*

(Received 14 December 2004; accepted 25 January 2005; published online 7 March 2005)

Unusual stress behavior was observed in W-incorporated hydrogenated amorphous carbon films prepared by a hybrid process composed of ion-beam deposition and magnetron sputtering. As the tungsten concentration increased from 0 to 2.8 at.%, the residual compressive stress decreased by 50%, without significant deterioration in the mechanical properties. This was followed by a rapid increase and a gradual decrease in the residual stress with increasing W concentration. High-resolution transmission electron microscopy analysis and first-principle calculations show that the reduced directionality of the W–C bonds in the W-incorporated amorphous carbon matrix relaxes the stress caused by the distorted bonds. © 2005 American Institute of Physics. [DOI: 10.1063/1.1883328]

Alloying hydrogenated amorphous carbon (*a*-C:H) films with transition metals, such as Ti, Mo, Cr, or W, have been one of the most common strategies to reduce the high residual compressive stress of *a*-C:H film.^{1–5} In addition to reducing the stress, the incorporation of the metal atoms results in the formation of nanocomposite films composed of metal carbide moieties encased within an amorphous carbon matrix.^{1–6} Furthermore, metal incorporation is known to enhance the chemical affinity of the films to metallic substrates, which improves the film's adhesion.^{7,8} However, the cause of the reduction in stress resulting from metal incorporation is not yet fully understood. One of the difficulties is that the atomic bonding within the amorphous carbon matrix varies with metal incorporation.^{3,9,10} It was, therefore, hardly possible to investigate an indisputable effect of metal incorporation on the properties of a deposited film.

In the present work, we investigated the effect of W incorporation without invoking any structural change in the amorphous carbon matrix. The residual compressive stress decreased dramatically with increasing W concentration when the incorporated tungsten atoms were dissolved in the amorphous carbon matrix without forming a WC_{1-x} phase. First-principle calculations elucidated the role of the dissolved W atoms, in that the W–C bond has a much weaker bond directionality than that of the C–C bond, which reduces the stress resulting from bond distortion. Further incorporation of W led to a rapid increase in the residual stress, followed by a gradual decrease as the crystalline WC_{1-x} phase evolved.

Using a hybrid deposition system composed of a hydrocarbon ion beam and a tungsten dc magnetron sputter, 300 nm thick W-incorporated *a*-C:H films were deposited on Si wafers. Benzene was supplied to an end-Hall-type ion gun to generate a flux of energetic hydrocarbon ions, whereas argon sputtering gas was supplied to the W dc magnetron sputtering source. During the deposition process, a

radio frequency self-bias voltage of –200 V was applied to the substrate. The composition of the films was characterized using Rutherford backscattering spectrometry and elastic recoil detection techniques. The W concentration of the films could be controlled in the range of 1.9–8.6 at.% by changing the Ar:C₆H₆ flow rate within the range of 0.57–0.9. The hydrogen concentration in the films decreased monotonically from 33.7 to 30.2 at.% in this composition range. The residual stress in the film was calculated from the curvature of the film/substrate composite using Stoney's equation. Nanoindentation was employed to characterize the mechanical properties of the film. The microstructure and atomic bond structure of the films were investigated using grazing incidence x-ray diffraction (GIXRD) and high-resolution transmission electron microscopy (HRTEM) with a dedicated parallel electron energy loss spectroscopy (EELS) attachment.

Figure 1 shows the dependence of the residual compressive stress in the film on the concentration of W. The residual stress exhibited an unusual behavior with increasing W incorporation, when the W concentration was <3.6 at.%. As the W concentration increased from 0 to 2.8 at.%, the residual compressive stress decreased monotonically from

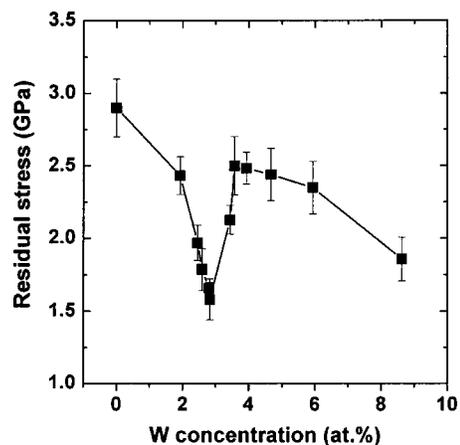


FIG. 1. Dependence of the residual compressive stress of the W-incorporated *a*-C:H films on the concentration of tungsten.

^{a)}Also at: School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea.

^{b)}Electronic mail: krlee@kist.re.kr

^{c)}Also at: Nano-Materials Research Center, Korea Institute of Science and Technology, P.O.Box 131, Cheongryang, Seoul 130-650, Korea.

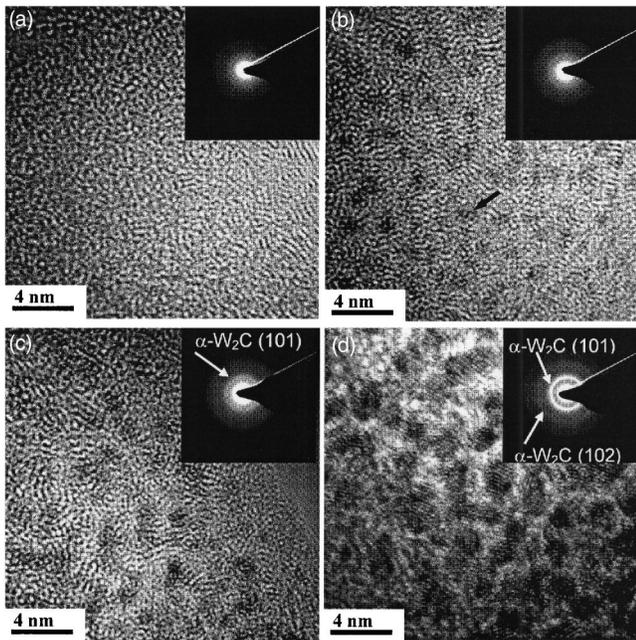


FIG. 2. HRTEM images and selected area electron diffraction patterns of a -C:H films with various W concentrations: (a) 1.9, (b) 2.8, (c) 3.6, and (d) 8.6 at. %.

2.9 to 1.5 GPa. However, the residual compressive stress increased rapidly to 2.5 GPa upon further incorporation of tungsten. Beyond a W concentration of 3.6 at.%, the residual compressive stress gradually decreased to a value of 1.9 GPa at a W concentration of 8.6 at.%, as has been observed in previous work on metal-incorporated diamondlike carbon films.^{4,10–12} In contrast to the observed residual stress behavior, the hardness of the films gradually decreased from 23.5 to 19.5 GPa with increasing W concentration from 0 to 8.6 at.%. Therefore, it was possible to fabricate a film with a reduced residual stress without observing any associated degradation of the film's mechanical properties.

Figure 2 shows HRTEM microstructures for various W concentrations. Insets of the figures are the selected area electron diffraction patterns obtained from the samples. At a W concentration of 1.9 at. % [Fig. 2(a)], only an amorphous granular structure, with diffuse halos in the diffraction pattern, was observed. This microstructure is essentially the same as that of a pure a -C:H film, showing that all the incorporated W atoms were dissolved in the amorphous carbon matrix. For a W concentration of 2.8 at.%, localized dark regions with a diameter of about 1 nm appeared in the transmission electron microscopy microstructure, as indicated by the arrow in Fig. 2(b). The dark region eventually evolved into a crystalline WC_{1-x} phase as the W concentration increased. However, both the electron diffraction patterns and the GIXRD spectra showed that the crystalline phase was yet to be evolved. WC_{1-x} crystallites started to appear at W concentrations >3.6 at.%, where a noticeable diffraction ring was observed, as shown in Fig. 2(c). The degree of crystallinity and size of the WC_{1-x} crystallites increased with increasing W concentration. Figure 2(d) shows that WC_{1-x} crystallites with a diameter of about 2 nm were dispersed in the amorphous carbon matrix for a W concentration of 8.6 at.%. This structural change with increasing W concentration was also confirmed by the GIXRD spectra, where a broad diffraction peak corresponding to crystalline

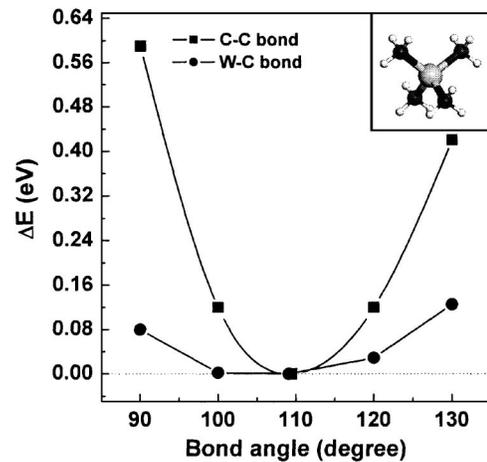


FIG. 3. The variation of total energy of C–C and C–W bonds as a function of distorted bond angle.

WC_{1-x} phase ($2\theta=37^\circ$) only appeared at W concentrations >3.6 at. %.

Even though the evolution of the WC_{1-x} phase was strongly dependent on the W concentration, the structure of the matrix was not affected by W incorporation as confirmed by high-resolution carbon K -edge EELS spectra of the matrix. The ratio of the peak near 286 eV ($C 1s \rightarrow \pi^*$ state) to the peak at about 295 eV ($C 1s \rightarrow \sigma^*$ state) was used to characterize the atomic bond structure of the matrix.^{13,14} The ratio was 0.55 ± 0.1 regardless of the W concentration, which suggests that the ratio of the sp^2 to sp^3 hybridized bonds does not vary with W incorporation.

The above results reveal that a close relationship exists between the residual compressive stress and the state of the W in the a -C:H films. A significant decrease in the residual compressive stress occurs when the incorporated W atoms are dissolved in the amorphous carbon matrix (for W concentrations <2.8 at. %). However, when the W atoms segregate to form an amorphous WC_{1-x} phase in the matrix, which occurs in the narrow W concentration range of 2.8–3.6 at. %, the residual compressive stress rapidly increases. A further increase in the W concentration results in the growth of nanosized WC_{1-x} crystallites in the matrix, which is accompanied by a gradual decrease in the residual stress. This gradual decrease in the residual stress is presumably due to an incoherent stress relaxation,¹⁵ and in other work, it has been discussed in terms of a percolation structural transition from an a -C:H-rich structure to a carbide-rich structure.^{3,10}

To understand the mechanism of the stress reduction caused by the dissolution of tungsten in the amorphous carbon matrix, we performed first-principle calculations on the total energy of the system with changes in bond angle. A schematic drawing of the system used in our calculations is shown in inset of Fig. 3. The four carbon atoms are arranged as a tetrahedron, with a carbon or tungsten atom located at the center. For simplicity, unbound carbon bonds were passivated by hydrogen atoms. The total energy of the system was calculated using one of the bond angles being distorted from the equilibrium angle of tetrahedral bond (109.5°) over the range of 90 – 130° . The DMOL³ computational software package was employed in our calculations.¹⁶ The wave functions were expanded using a double-zeta polarization basis set. In the absence of W, the total energy increased rapidly as

the bond angle deviated from the equilibrium value of the tetragonal bond. However, with a W atom located at the center of the tetrahedron, the increase in the total energy due to the distortion in bond angle was significantly reduced. This result suggests that W atoms in an amorphous carbon matrix play the role of a pivotal site, where distortion of the atomic bond angles can occur without inducing a significant increase in the elastic energy.

In summary, the residual stress of W incorporated *a*-C:H film is significantly dependent on the state of the incorporated W atoms. Pivotal action of W atoms in the amorphous carbon matrix reduces the strain energy arising from the distortion of the bond angles. However, segregation of the W atoms increased the residual stress significantly. At higher W concentrations, the nanosized WC_{1-x} crystallites evolved resulting in a gradually decrease in the residual compressive stress.

This research was supported by a grant (Code No.: 04K1501-01110) from the Center for Nanostructured Materials Technology under the 21st Century Frontier R&D Program of the Ministry of Science and Technology, Korea and the J&L Tech Co. Ltd.

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