Effect of Substrate Bias on Structure and Properties of W incorporated Diamond-like Carbon Films

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ABSTRACT

W incorporated diamond-like carbon (W-DLC) films were deposited on silicon (100) wafers by a hybrid deposition method combining ion beam deposition of carbon with DC magnetron sputtering of tungsten. During the films deposition, a wide range of negative bias voltage from 0 to −600 V was applied. W concentration in the film could be controlled by varying the Ar/C₆H₆ ratio in the supplying gas. In the present experimental condition, WC₁₋ₓ nano-sized particles were not observed in the amorphous carbon matrix. Regardless of the W concentration in the film, it was found that the G-peak position of the Raman spectra had a lowest value at a bias voltage of −200 V, which represents the highest sp³ bond fraction in the film. The highest residual stress, hardness and Young’s modulus were also observed when the bias voltage was −200 V. This result shows that the mechanical properties of W-DLC films were mainly dependent on the atomic bond structure of carbon. On the other hand, the electrical resistivity significantly decreased by the W incorporation.

INTRODUCTION

After Aisenberg et al. firstly reported the synthesis of diamond-like (DLC) carbon films using a low energy carbon ion beam [1], significant progress in the understanding the growth process of DLC films has been achieved in the last three decades. One noteworthy feature is that the incorporation of metallic components (Ti, W, Ag, Cu, Si, Au etc.) or other third elements (N, Ar, B) is used to overcome the shortcomings of DLC films such as high residual compressive stress, poor thermal stability and ductility [2-12]. Earlier studies on the third element addition showed a considerable improvement of the physical properties of the metal containing DLC films (Me-DLC). Recently, nanocomposite films composed of nano-sized particulates dispersed in the matrix phase drew much attention due to its potential of unique properties. Nevertheless, the size, volume fraction and distribution of the nanometer metallic particulates formed in the films must be optimized carefully [13].

In the present work, we report the deposition behavior of W incorporated DLC (W-DLC) films. It is widely accepted that the Me-DLC films consist of the embedded nanometer metallic particulates (if metal formed carbides) and amorphous carbon or hydrocarbon matrix. However, we focus on the deposition behavior of the films at low W concentration where WC₁₋ₓ particulate phase does not form. The dependence of the structure and properties of the deposited film on the negative bias voltage are studied by a comprehensive set of experiments. We confirm that the W
incorporation does not change the deposition mechanism of the DLC films. This result is useful for understanding the structure and the properties of WC-C nanocomposite films of high W concentrations [14].

**EXPERIMENTAL**

W-DLC films were prepared by a novel hybrid deposition system consisting of a DC magnetron sputter gun of W target (high purity 99.95 %) and an end-Hall type ion gun. C6H6 was supplied to the ion gun for the carbon film deposition. W concentration in the film was varied by changing the Ar fraction of the reaction gas in the range of 65~85%. The base pressure was kept less than 2×10^{-4} Pa, but the deposition pressure ranged from 0.08 to 0.133 Pa depending on the Ar fraction. A p-type Si (100) wafer of thickness 500±10 µm was used as the substrate. A thin Si wafer of thickness 200±10 µm was also used to measure the residual compressive stress of the film. The deposition rate of the film decreased with increasing Ar fraction. The deposition time was adjusted to obtain films of thickness 350±60 nm. A substrate bias voltage ranging from 0 to –600 V in DC was applied by a medium frequency (250 KHz) power supply. For ease of comparison, a series of pure DLC films were also deposited by the ion beam method without operating the sputter gun.

The W concentration in the film was evaluated by RBS using a collimated 4He^{2+} ion beam of 2 MeV. The film thickness was measured by an Alphastep-200 profilometer. The microstructures of the films were characterized by micro-Raman spectroscope using a 514.5 nm Ar^+ laser. The mechanical properties were measured by the nano-indentation technique in a continuous stiffness measurement (CSM) mode with a maximum indentation depth of 350 nm. The characteristic hardness of the film was chosen in the depth where the measured value is not affected by the soft Si substrate. The residual stress of the film was calculated from the curvature of the film/substrate composite using the Stoney equation. The electrical resistivity of the film was measured by a four-point probe system (1.0 mm equal probe spacing).

**RESULTS AND DISCUSSION**

Typical RBS spectra of the W-DLC films deposited at the substrate bias voltage of –200 V are shown in figure 1. The spectra show that the W concentration increased with increase of Ar fraction. The W concentration in the film increased from 2.9 to 8.5 at.\% as the Ar fraction in the supplying gas increased from 65% to 85% (figure 2). In the present concentration range, the WC_{1-x} crystalline phase was not observed in the film as confirmed by the grazing incidence x-ray diffraction (GIXRD) method. It must be noted that the W concentration was mainly dependent on the Ar fraction. Even if the applied bias voltage slightly varied the W concentration, the variation was limited to ±0.5 at.\% in the range of the bias voltage from 0 to –600 V.

Figure 3 shows the residual compressive stress of the film as a function of the bias voltage. W incorporation into DLC films considerably reduced the residual compressive stress, especially
when the negative bias voltage was small. The residual compressive stress decreased from 2.27 to 0.58 GPa when the negative bias voltage was 0 V. As the negative bias voltage increased, the reduction in the residual stress became less significant. When the negative bias voltage was –600V, the reduction in the residual stress caused by the W incorporation was not observed. As in the pure DLC film, the residual stress of the W-DLC has a maximum at –200 V for all W concentrations. This behavior can be explained by a simple model by Davis for the ion bombardment phenomena during thin film deposition [15]. This model suggests that the compressive stress is mainly balanced by the knock-on processes causing the stress formation and the thermal spike effect causing the stress relaxation in the film. A maximum residual stress, as observed in the present work, was successfully predicted by the kinetic model.

Mechanical properties of the film exhibited similar behavior. The dependence of the film hardness on the bias voltage is summarized in figure 4. The maximum hardness was observed at a bias voltage of –200 V regardless of the W concentration. The plane strain modulus of the film exhibited the same dependence on the negative bias voltage. These results show that the mechanical properties and the residual compressive stress of the W-DLC film are determined by the same structural factors. It must be noted that when W is incorporated in the film without forming WC_{1-x} particulates, the structure-property relationship was essentially the same as that in pure DLC film.

Figure 5 shows the representative Raman spectra of the deposited WC-C films as a function of the bias voltage when the W concentration was 2.9 at.%. In the range of 1100~1700 cm\(^{-1}\), there is a broad asymmetric Raman scattering band, representing the typical characteristic of DLC film. We found that the intensity of the Raman spectra decreased with increasing bias voltage. However, the reason for this phenomenon is yet to be resolved. The Raman spectrum analysis of amorphous carbon includes deconvolution of the spectrum with two Gaussian peaks: the G and D peaks. The atomic bond structure of the film is characterized by the intensity ratio,
the full width at half maximum (FWHM) values, or the position of each peak. In the present work, G-peak position was used to qualitatively compare the atomic bond structure, since the error in G-peak position was much smaller than other characteristics. The G-peak positions as a function of bias voltage are shown in figure 6. It was reported that the G-peak position shifted upward due to the residual compressive stress by 4.1 cm$^{-1}$/GPa [17]. G-peak position in figure 6 was after the correction of the residual stress effect. It is obvious that the G-peak position runs through a minimum at $-200$ V and then increases with further increment of the bias voltage. In addition, increasing W incorporation also resulted in an increase of the G-peak position. Since the lower G-peak position represents a higher fraction of sp$^3$ carbon bonding [17, 18], it can be said that the film deposited at the bias voltage of $-200$ V has the highest fraction of sp$^3$ carbon bonding.

**Figure 3.** The residual compressive stress of the films as a function of the bias voltages.

**Figure 4.** The hardness of the films as a function of the bias voltages.

**Figure 5.** Representative Raman spectra of the deposited films as a function of bias voltage.

**Figure 6.** Dependence of G-peak position on the negative bias voltage for various W concentrations.
bond. This result shows that the residual compressive stress and the mechanical properties are closely related to the sp³ hybridized bond. The mechanical properties of carbon materials are dependent on the degree of 3-dimensional interlinks of the atomic bond network. For example, atomic bonds in diamond are fully interlinked in 3-dimensions while for graphite 2-dimensional graphitic planes are bonded by a weak Van der Waals force. High content of sp³ hybridized bond would increase the 3-dimensional interlinks, resulting in the high hardness and elastic modulus. However, increasing 3-dimensional interlinks in amorphous carbon also increases the distortion of the carbon bond, which causes the high residual stress because the covalent bond is highly directional. It is worth noting that the carbon bond network mainly determined the mechanical properties of W-DLC film even if a significant amount of W was incorporated.

However, W incorporation significantly decreased the electrical resistivity as shown in figure 7. The resistivity of the film decreased by a factor of 3-5 due to W incorporation. (The resistivity of pure DLC films is in the order of 10⁷ Ω cm.) This result shows that the W incorporation changed the electronic band structure. It is also noted that the G-peak position shown in figure 6 shifted upward with increasing W concentration. Hence, the W incorporation also increased the sp² hybridized bond that can increase unpaired π electrons. At a fixed W concentration, increasing the bias voltage further decreased the resistivity. This decrease would be due to the change in the atomic bond structure from the diamond-like phase to the graphitic one. This result shows that the W incorporation can control the electrical properties without causing considerable changes in the carbon bond structure or the mechanical properties.

CONCLUSIONS

W-DLC films were deposited using a novel hybrid deposition system composed of DC magnetron sputtering and an end-Hall ion gun source. The dependence of the atomic bond structure and the mechanical properties on the negative bias voltage and W concentration were comprehensively studied. For all negative bias voltages, increasing W concentration decreased the content of sp³ hybridized bonding. However, the Raman analysis proposed that the highest content of sp³ hybridized bond was obtained at a negative bias voltage of −200 V, where the maximum in the residual compressive stress, the hardness and the elastic modulus of the film were also observed. Despite a significant addition of W, the mechanical properties of the deposited W-DLC films are mainly dependent on the changes in the atomic bond structure of
carbon. The mechanical properties of WC-C nanocomposite film are discussed in terms of the present experimental results [14]. W incorporation made it possible to control the electrical resistivity without a considerable change in the mechanical properties of the W-DLC films.

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