Metal-containing diamond-like carbon with self-assembled alternating nano-scaled layers

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Introduction

Metal-containing diamond-like carbon (Me-DLC) thin films exhibiting alternating layered structure provide improved wear resistance due to the existence of terminating cross-sectional cracks and dislocations. [1-5] In order to obtain alternating layered structures, many physical vapor deposition (PVD) processes have been used. Alternating layers of W/C, [6] Mo/C, [7] WC/C, [8] and Ti/C [9] were obtained using magnetron sputter deposition techniques, in which two targets of carbon and the pertinent metal were used. Binary targets of tungsten and carbon were also used in a magnetron deposition technique to obtain alternating layers of WC/C under oscillating atmospheres of Ar and Ar/CH_4 mixture. [10] TiC/C, WC/C, Ti/C, and Al/C alternating layers were obtained using various elemental sources in arc deposition processes. [11, 12] Two targets of nickel and carbon were used in a pulse laser deposition to obtain alternating layers of Ni/C. [13, 14] All the above processes involve the use of more than one type of target materials. On the other hand, a single target of tungsten and tungsten carbide were used in a laser deposition process to obtained alternating layers of W/C and WC/C, respectively. [15, 16] However, the occurrence of the alternating layers was due to substrate rotation.

It therefore appears that multiple targets are required for the growth of alternating layers. However, in the paper, we report the use of a single target in a magnetron sputter deposition to grow Me-DLC thin films having self-assembled alternating nano-scaled layers in various CH_4 concentrations. The target materials used in the sputter deposition include Pt, Cu, and Ni. It was found that the periodicities of the layered structure range from 10^0 nm to 10^1 nm. The appearance of alternating layers and the periodicity depend on both the type of the target materials and the deposition conditions. Based on the consideration of the deposition rate and the catalytic reaction of metal, the formation such self-assembled alternating nano-scaled layers is explained.

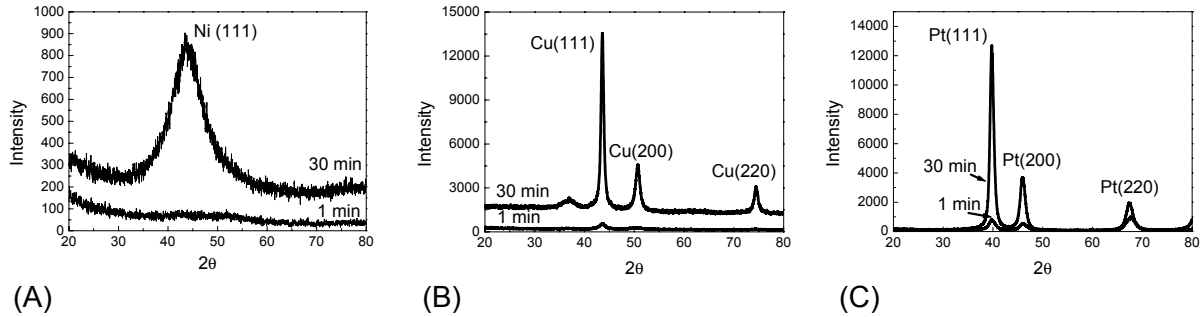
Experimental

In this study, we have used a dc reactive sputter deposition system equipped with one single magnetron gun to deposit self-assembled alternating layers of several Me-DLC thin films. The target materials used include nickel (99.99%), platinum (99.99%), and copper (99.95%). Single crystal wafers of (100) Si were used as the substrates. To deposit the Me-DLC thin films, the sputter deposition chamber was first evacuated to a pressure lower than 5×10^{-5} torr and then back-filled with an argon/methane gas mixture to a desired deposition pressure of 1×10^{-2} torr. The distance between the target and the substrate was maintained at 40mm. Both the Ar/CH_4 ratio and the deposition time were

varied. The substrates were not heated or rotated during the deposition under all the conditions. After the deposition, surface morphologies and cross-sectional views of Me-DLC thin films were examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Deposition rates of Me-DLC films were determined from the thicknesses measured on the cross-section images. Crystallinity and microstructure of the Me-DLC thin films were investigated using grazing incident x-ray diffraction (GIXD) and TEM, respectively.

Results and Discussion

GIXD spectra of the 1-min and 30-min Me-DLC (Me = Ni, Cu, or Pt) thin films are given in Fig. 1. For the 1-min samples, it appears that the carbons in all the thin films exhibit an amorphous structure. The spectra of 1-min thin films also indicate that nickel has worst crystallinity, copper has a better crystallinity than nickel, and platinum has the best crystallinity. As the deposition time increases to 30 min, the crystallinity of all the metal improves, while the carbon still exhibits an amorphous structure. It is believed that a sufficient amount of metal is required to allow the formation of crystalline structure.



(A) (B) (C)

Fig. 1. Low angle XRD spectra of (A) Ni-DLC, (B) Cu-DLC, and (C) Pt-DLC thin films.

From the SEM cross section images, the deposition rates of Me-DLC were determined. The results are given in Fig. 2. It is seen that Cu-DLC films has the highest growth rate, followed by Pt-DLC and then Ni-DLC. The normalized deposition rates for Cu-DLC, Pt-DLC, and Ni-DLC are respectively 1, 0.71, and 0.49. In a previous study, we have found that metallic concentration increases with growth rate, regardless of the metal type. [24] This indicates that the growth rate is primarily dominated by the metal deposition. As a result, it is believed that the sputtering yield (SY) and the thermallization distance (D) of a metal dominate the growth. The normalized SY of Cu, Pt, and Ni are respectively 1, 0.43, and 0.43, while the normalized D values are respectively 1, 1.8, and 1. A figure of merit (FOM) was then defined as FOM = SY x D. A larger value of FOM means a higher deposition rate. The values of FOM for Cu, Pt, and Ni are calculated to be 1, 0.77, and 0.43, respectively. The values of FOM are in a very good agreement with the normalized deposition rates, i.e., 1, 0.71, and 0.49 for Cu-DLC, Pt-DLC, and Ni-DLC, respectively.

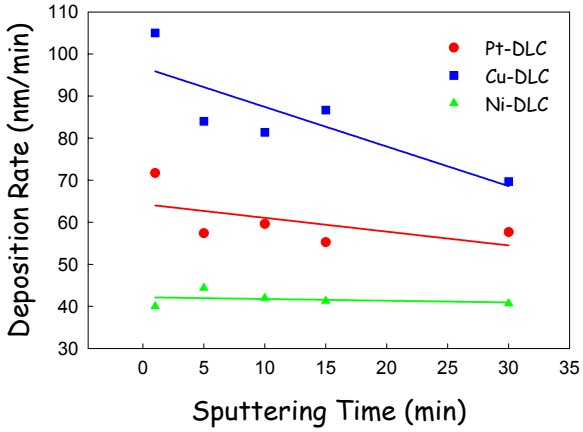


Fig. 2. The deposition rate plot of Me-DLC films.

Despite of the differences in the crystallinity and the deposition rate, a series of Me-DLC films with alternating nano-scaled layers were obtained. Fig. 3 is a Ni-DLC thin film with an alternating layered structure. The alternating layered structure begins at the film/substrate interface and continues to the film surface. In a period, there are a metal-rich layer and a carbon-rich film. The appearance of alternating layered structure and the periodicity, however, depend on the type of metals used and the deposition parameters. Fig. 4 shows TEM cross section images of Ni-DLC, Cu-DLC, and Pt-DLC films. These films were obtained under the same deposition condition of 100 W dc power, CH_4 66.7%, and 1 x 10^{-2} torr. As shown in Fig. 4A, there is no alternating layered structure found in the Ni-DLC film. The Ni-DLC film has a microstructure in which nano-sized Ni particles are embedded in the DLC matrix, representing a periodicity of infinite. On the other hand, alternating layered structure is clearly seen in both Cu-DLC film (Fig. 4B) and Pt-DLC film (Fig. 4C). The periodicities are 13 nm and 11 nm, respectively, for Cu-DLC film and Pt-DLC film. As the CH_4 concentration decreases, an alternating layered structure appears in Ni-DLC film. Fig. 5 shows TEM cross section images of Ni-DLC, Cu-DLC, and Pt-DLC films obtained at a lower CH_4 concentration of 40%. It is obvious that all the Me-DLC thin films exhibit alternating layered structures. The periodicities are 15 nm, 16 nm, and 22 nm, respectively, for Ni-DLC film (Fig. 5A), Cu-DLC film (Fig. 5B), and Pt-DLC film (Fig. 5C).

The growth mechanism of self-assembled alternating layered structure has not yet been well understood. We discuss the appearance of alternating layers based on the consideration of the deposition rate and the catalytic reaction of metal. In a previous study, we have found that all three Me-DLC thin films exhibit higher deposition rates than DLC thin films, indicating higher deposition rates for metals, suggesting a high deposition rate for a metal than carbon. [17] Therefore once the deposition begins, more metal would be deposited on the substrate than carbon would. As a result, a metal-rich layer starts to grow. While the deposition process proceeds, the metal-rich layer thickens, indicating more metal accumulation. At a time when the amount of metal reaches a certain value, the metal behaviors as a catalyst to promote the deposition of carbon, as in the growth of carbon nanotubes. [18] At this time, more carbon deposit

beings, leading to the formation of a carbon-rich layer. It was found that an appropriate amount of metal catalyst is required for the formation of carbon nanotubes. [19] The fact that a sufficient amount of metal is required seems to indicate the formation of micro-crystalline metal is necessary. [20] In the present study, the amount of metal needed for the catalytic reaction is not known as it depends simultaneously on several factors such as the metal type, the interaction of the metal with the carbon in the metal-rich layer, and the growth condition. The growth of the carbon-rich layer would then progressively shadow the catalyst reaction of the metal in the metal-rich layer underneath. Without the catalyst reaction, the deposition of metal becomes faster than the carbon again. As a result, a metal-rich layer appears again and, while the growth continues, is followed by a carbon-rich layer as before. Continuous growth would then allow the periodic appearance of metal-rich/carbon-rich layers. Self-assembled alternating layered structure is thus obtained. Finally, it was also found that the deposition rate of Ni is the lowest among all three metals and decreases with the argon concentration during the reactive sputter deposition. [17] Therefore at a low argon concentration, e.g., 50%, carbon deposition rate becomes comparable with Ni deposition rate. As a result, no alternating layer forms, but a film microstructure in which Ni particles are embedded in DLC matrix is obtained, as shown in Fig. 4A.

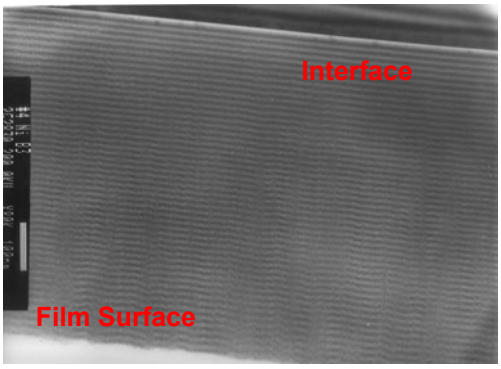
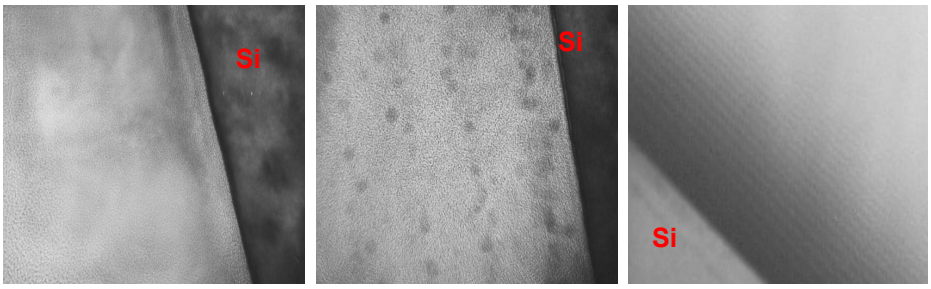


Fig. 3. TEM cross sectional image showing alternating layered structure in a Ni-DLC film.



(A) —10nm (B) — 10nm (C) — 50nm

Fig. 4. TEM cross sectional images of (A) Ni-DLC film, (B) Cu-DLC film, and (C) Pt-DLC film. These films were obtained using a power of 100 W, CH_4 concentration 66.7%, and a pressure of 1×10^{-2} torr.

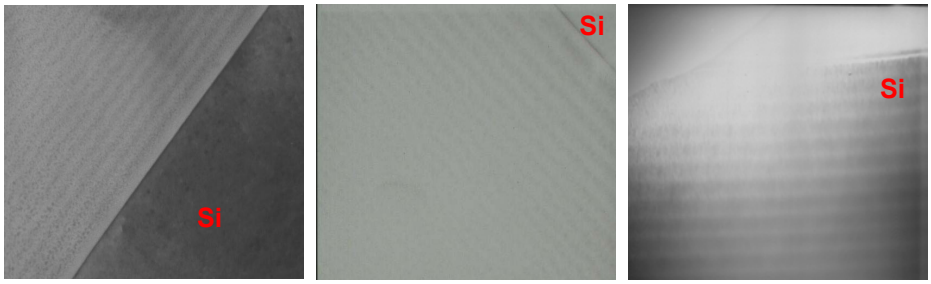


Fig. 5. TEM cross sectional images of (A) Ni-DLC film, (B) Cu-DLC film, and (C) Pt-DLC film. These films were obtained using a power of 100 W, CH_4 concentration 40%, and a pressure of 1 x 10^{-2} torr.

Conclusions

Me-DLC thin films (Me = Ni, Cu, or Pt) exhibiting self-assembled alternating nano-scaled layers were obtained using magnetron sputter deposition. Unlike previous works where multiple targets were used, we have used only a single sputter gun during the deposition. The carbons in all the films obtained exhibit an amorphous structure. In the mean time, depending on the deposition condition, different metals show different degrees of crystallinity. In general a sufficient amount of metal is required to allow it to form crystalline structure. The amount required depends on the metal type and the deposition condition. The type of metals was also found to influence the deposition rate. The values of FOM are in a very good agreement with the normalized deposition rates. Despite of the differences in the crystallinity and the deposition rate, a series of Me-DLC films with an alternating layered structure were obtained. In a period, there are a metal-rich layer and a carbon-rich film. The appearance of alternating layered structure and the periodicity, however, depend on the type of metals used and the deposition parameters. The appearance of alternating layers is discussed based on the consideration of the deposition rate and the catalytic reaction of metal.

Acknowledgement

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