Self-assembled Alternating Nano-scaled Layers

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ABSTRACT

This paper reports the use of a conventional sputter deposition technique to produce self-assembled alternating nano-scaled layers consisting of diamond-like carbon (DLC) and metal. A conventional sputter deposition technique produces alternating layers only when multiple sputtering targets are employed. However, we have successfully demonstrated that the use of only one single sputtering gun in a conventional sputter deposition process could lead to the formation of alternating nano-scaled layers through self-assembling. The microstructure of the alternating layers was examined as a function of the deposition parameters.

Keywords: self-assembling, layered structures; diamond-like carbon; thin films, sputter deposition

1. INTRODUCTION

It is known that diamond-like carbon (DLC) exhibit excellent tribological properties especially against steel [1,2]. Many techniques have been used for the preparation of Me-DLC thin films [3-10]. However, high internal stresses and insufficient adhesion of DLC films to the substrate have also been found to limit their applications. Therefore, metallic elements were introduced into DLC films reduce the stresses and enhance the adhesion [5,6]. It has been shown that the metallic component in an Me-DLC thin film forms nanosized clusters that distribute homogeneously in the DLC matrix [11,12]. Recently, alternating layers of carbon and metal or metal carbide were observed in W-DLC thin film [13,14]. Such an alternating layered structure was found to have better wear and fatigue resistance. A reactive dc unbalanced multiple-target magnetron sputter deposition technique with moving substrate was used for the growth of the W-DLC thin films. A total of four magnetron guns with two different types of target materials were used in the studies reported in Refs. 13 and 14. In this study, we report the use of a dc reactive sputter deposition system equipped with only one single magnetron gun to deposit self-assembled alternating layers of Me-DLC thin films.

2. EXPERIMENTAL

The target materials used in the sputter deposition system include nickel (99.99%), platinum (99.99%), and copper (99.95%). Single crystal wafers of (100) Si were used as the substrates. For the film deposition, the sputter deposition chamber was first evacuated to a pressure lower than 5 x 10^{-5} torr and then back-filled with an argon/methane gas mixture to a desired deposition pressure of 1x10^{-2} torr. The electrode distance was 40mm. The deposition time varied from 1min to 30min. The substrates were not heated during the deposition under all the conditions. Compositions of the resulting Me-DLC thin films were examined using energy dispersive spectrometry (EDS). Surface morphologies and cross-section views of Me-DLC thin films were examined using scanning electron microscopy (SEM). Deposition rates of Me-DLC films were determined from the thickness measured on the SEM cross-sectional images. Crystallinity and microstructure of the Me-DLC thin films were investigated using grazing incident x-ray diffraction (GID), transmission electron microscopy (TEM), and micro-Raman microscopy.

3. RESULTS AND DISCUSSION

Me-DLC (Me = Ni, Cu, or Pt) thin films were obtained. The crystallinity was first examined using GID. It was found that in general the carbons in the films are amorphous while the metals exhibit polycrystalline structure, as shown in Fig. 1. However, it appears that Ni has a worse degree of crystallinity, and both copper and platinum have a better degree of crystallinity. Occasionally, a minor amount of polycrystalline nickel carbide was also found in Ni-DLC. By increasing the deposition time, i.e., increasing the thickness, the crystalline of the metals can be improved.

The thickness of these thin films is in the order of 10^2 nm. Most of the films obtained exhibit alternating layered structures, which can be seen in TEM micrographs. Regardless of the film thickness, the alternating layered structure starts at the film/substrate interface and continues to the film surface. This is shown in Fig. 2. In a period, there are a metal-rich layer and a carbon-rich film. The occurrence of alternating layered structure and the periodicity, however, depend on the type of metals and the deposition parameters used. TEM analysis was performed to examine the cross sections of Ni-DLC, Cu-DLC, and Pt-DLC films prepared using a power of 100 W, an Ar/CH_4 ratio of 1, and a pressure of 1 x 10^{-2} torr. It was found that there is no alternating layered structure in the Ni-DLC film. The film exhibits a microstructure in which the nano-sized Ni particles are embedded homogeneously in the DLC matrix. On the other hand, alternating layered structure is clearly seen in both Cu-DLC film and Pt-DLC film prepared using the same conditions. The periodicities are 13 nm and 10 nm, respectively, for Cu-DLC film and Pt-DLC film. However, as the Ar/CH_4 ratio increases, alternating layered structure appears in Ni-DLC film. It was then observed that all the Me-DLC thin films prepared using a power of 100 W, an

Ar/CH_4 ratio of 3, and a pressure of 1 x 10^{-2} torr exhibit alternating layered structure. The periodicities are 15 nm, 15 nm, and 22 nm, respectively, for Ni-DLC film, Cu-DLC film, and Pt-DLC film.

4. CONCLUSION

Thin films with alternating layered structures are normally produced in a conventional sputter deposition technique by using multiple sputtering targets. However, we have successfully demonstrated that the use of only one single sputtering gun in a conventional sputter deposition process could lead to the formation of alternating nano-scaled layers through self-assembling. The thickness of these thin films is in the order of 10^2 nm. Regardless of the film thickness, the alternating layered structure starts at the film/substrate interface and continues to the film surface. The occurrence of alternating layered structure and the periodicity, however, depend on the type of metals and the deposition parameters used.

Finally the Raman spectra were investigated for Cu-DLC specimens. Both the D-band and G-band were detected a 41.6 at% Cu-DLC thin film. It was further found that the I_D/I_G ratio increased with Cu concentration, indicating a smaller carbon cluster size at a higher Cu concentration. This would have given a larger full width at the half maximum (FWHM). However, the FWHM decreases with the Cu concentration, suggesting that through the addition of copper the film stresses are greatly released. The stress relieve is strong enough to overcome the effect of reducing carbon cluster size on the FWHM.

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REFERENCES

[1] K. Enke, Thin Solid Films 80 (1981) 227.

[2] T. Mori, Y. Namba, J. Appl. Phys. 55 (1984) 3276.

[3] K. Bewilogua, C.V. Cooper, C. Specht, J. Schroder, R. Wittorf, M. Grischke, Surf. Coating Technol. 127 (2000) 224.

[4] D.P. Monaghan, D.G.. Teer, P.A.. Logan, I. Efeoglu, R.D. Arnell, Surf. Coating Technol. 60 (1993) 525.

[5] K. Oguri, T. Arai, Surf. Coating Technol. 47 (1991) 710.

[6] Y.H. Wu, C.M. Hsu, C.T. Chia, I.N. Lin, C.L. Cheng, Diamond and Related Materials 11 (2002) 804.

[7] T. Hioki, Y. Itoh, A. Itoh, S. Hibi, J. Kawamoto, Surf. Coating Technol. 46 (1991) 233.

[8] Q. Wei, J. Sankar, J. Narayan, Surf. Coating Technol. 146-147 (2001) 250.

[9] G.Y. Chen, J.S. Chen, Z. Sun, Y.J. Li, S.P. Lau, Applied Surface Science 180(2001) 185.

[10] V. Rigato, G. Maggioni, D. Boscarino, G. Mariotto, Surf. Coating Technol. 116 (1999) 580.

[11] J.B. Pethica, P. Koidl, J. Vac. Sci. Technol. A3 (1985) 239.

[12] H. Dimigen, H. Hubsch, R. Memming, Appl. Phys. Lett. 50 (1987) 1056.

[13] K. Bewilogua, C.V. Cooper, C. Specht, J. Schroder, R. Wittorf, M. Grischke, Surf. Coating Technol. 127 (2000) 224.

[14] C. Strondl, N.M. Carvalho, J.Th.M. De Hosson, G.J.

van der Kolk, Surf. Coating Tech. 162 (2003) 288.

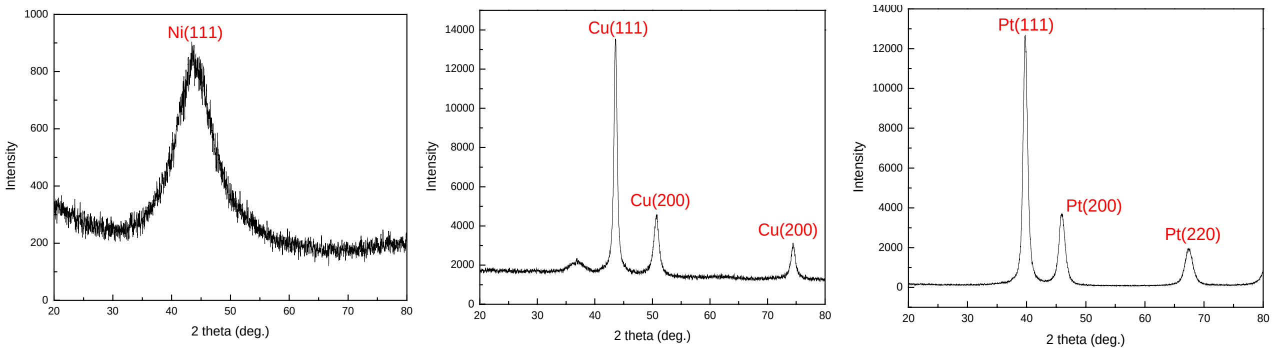

Fig. 1. Low angle XRD patterns of 1-min samples: Ni-DLC (top), Cu-DLC (middle), and Pt-DLC (bottom).

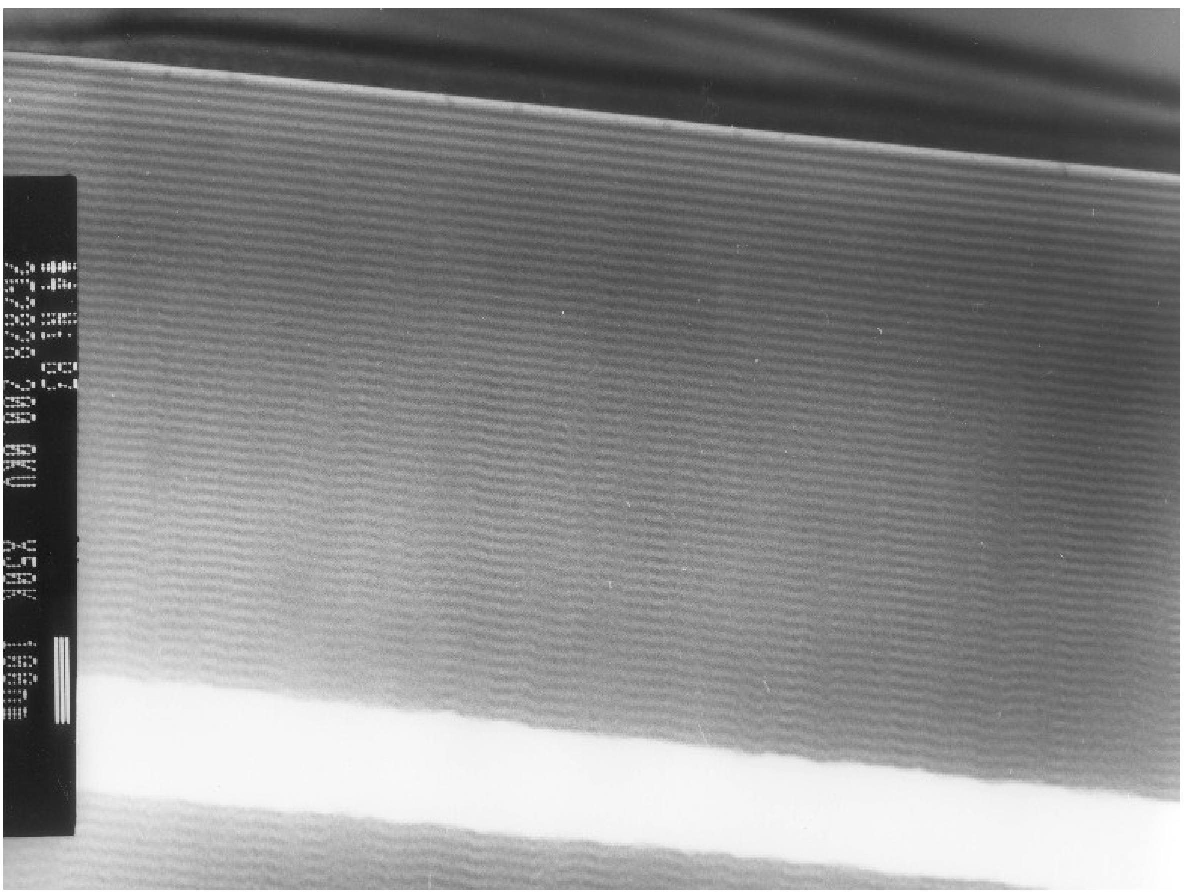

Fig. 2. TEM cross sectional image showing alternating layered structure in a Ni-DLC film.