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Microstructure and Physical Properties of Sputtered Metal Containing Nanocrystalline Structured Carbon Coatings

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Abstract

Metal containing hydrogen free nanocrystalline structured carbon (Me:nc-C) films were synthesized by closed-field unbalanced magnetron sputtering system (CFUBM). The aim of this study was to determine the relationship between the microstructure and physical properties of Me:nc-C films as a function of the concentration of materials. The film structures were examined by x-ray photoelectron spectroscopy and high resolution transmission electron microscopy. The physical properties of the Me:nc-C films were evaluated by using a 4-point probe. The fraction of graphite clusters was found to be increased by containing titanium and the electrical resistivity decreased with increasing amount of containing.

Keywords : Metal containing nanocrystalline structured carbon, Me:nc-C

1. Introduction

Carbon based coatings including DLC are widely utilized in many applications requiring multi-functional properties, such as high hardness, a high elastic modulus, a low friction coefficient, good chemical inertness and good surface roughness. In general, DLC films are known as insulators with an electrical resistivity in the range of 10^{10}~10^{13} Ω·cm, due to the high fraction of sp^3 bonds in the sp^3/sp^2 combined bonds [1-11]. However, highly conductive carbon films containing a large fraction of sp^2 bonds have recently been reported [8-11]. These films have the advantage that they can be used in a variety of industrial applications involving FPDs and various electronic devices, owing to their good conductive properties and, consequently, they have been intensively studied. The electronic structure of carbon depends mainly on the π states, because these states are located near the Fermi level. Therefore, one way of making highly conductive carbon film is to enhance the density of the sp^2-graphite π bonds by elemental doping.

In this study, we illustrate the relationship between the electrical properties and microstructure of metal containing nanocrystalline structured carbon (Me:nc-C) films synthesized by closed field unbalanced magnetron sputtering (CFUBMS). The electrical resistivity of nc-C films can be reduced down to 0.0002 Ω·cm by adjusting the amount of elemental doping. The corresponding mechanism is proposed for metal containing nc-C films, along with film analyses by XPS and HRTEM and the assessment of their physical properties.

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2. Experimental Details

Hydrogen free carbon films were deposited with various concentration of materials by CFUBMS. The schematic diagram of this system is shown in Fig. 1. The circular graphite cathode used for the magnetron sputtering was installed on one side of the chamber, while the metal sputtering source for the elemental doping was located on the opposite side. Magnetron sources were operated simultaneously in an argon atmosphere. The silicon (100) wafer substrates were heated to 150°C while being rotated, so as to alternately face the carbon and metal fluxes. The jig rotation speed was fixed at 24 rpm to prevent the formation

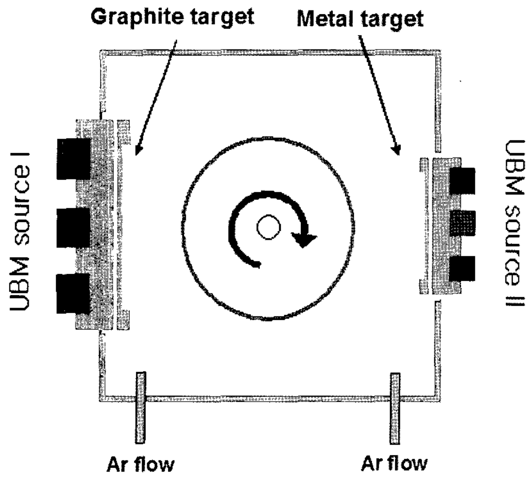


Fig. 1. Schematic diagram of the CFUBM system.

Table 1. Deposition conditions for Me:nc-C coatings

Conditions	Substrate bias (V)	Working pressure (Pa)	Graphite target power density (W/cm^2)	Me target power density (W/cm^2)
Ar plasma precleaning	−700	2.0	0	0
Me:nc-C coatings	−200	0.4	30	variable

Base pressure: 0.003 Pa.
Substrate temperature: 150°C Jig rotation speed: 24 rpm.
Target to substrate distance: 60 mm.

of laminated structures. The experimental conditions are listed in Table 1. The film thickness was kept at a constant value of 0.5 μm. Silicon (100) wafer was used as the substrate in the characterization of the microstructure and physical properties. The changes in the chemical state of the carbon films were studied using X-ray photoelectron spectroscopy (XPS). The film structures of the carbon films were investigated by High Resolution Transmission Electron Microscopy (HRTEM). The electrical resistivity of the film was measured by the 4-point probe method.

3. Results

3.1. Changes in the Chemical Bonding State of the Metal Containing Carbon Films

Table 2 shows the main peak intensity and position changes in the XPS spectra corresponding to the carbon 1s core peak for various amounts of titanium and gold contained. The peaks for the sp^2 carbon bonds are located at approximately 284.4 eV and those for the sp^3 carbon bonds are located at approximately 285.2 eV. In the carbon films containing titanium, no changes in the peaks were observed as the amount of doping was increased up to 2.5 at%Ti and the main peak was located at approximately 284.4 eV. Furthermore, the peak intensity increased with increasing amount of Ti doping. This indicates that these Ti containing nc-C films were composed of sp^2 carbon bonding clusters and that the fraction of sp^2 bonding in the sp^3/sp^2 combined bonds was increased by the doping with Ti. However, the further addition of titanium resulted in a shift in the carbon peak toward a higher wavelength. This can be interpreted as resulting from a change in the carbon bonding state and the formation of Ti-C bonds owing to the addition of titanium.

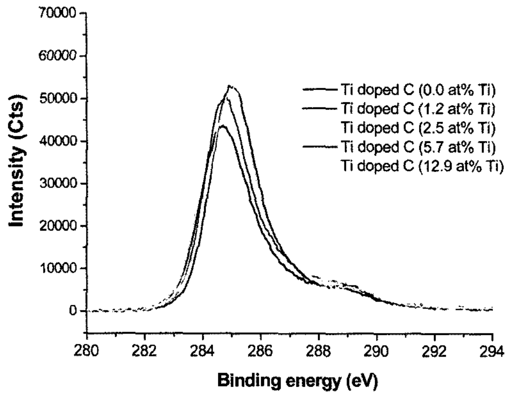
In the carbon films containing gold, no changes in the peaks were observed with increasing amount of Au adding, with the main peak being located at approximately 284.4 eV. However, a reduction in the main peak intensity occurred with increasing amount of Au doping. From these results, it can be suggested that no reaction occurred between the noble metal, Au, and the C atoms.

3.3. Microstructure of Metal Contianing Nanocrystalline Structured Carbon Films

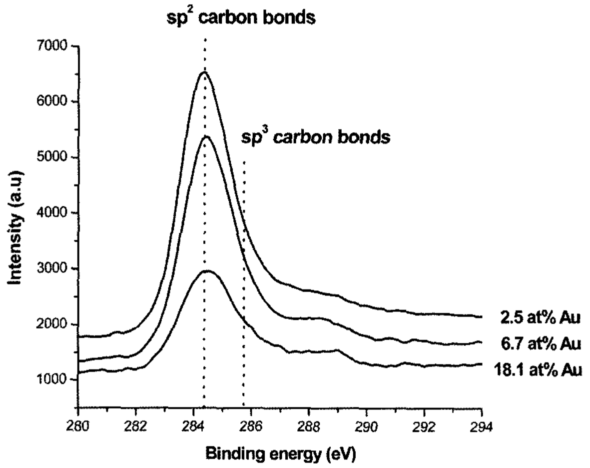
TEM analyses were performed to investigate the microstructure of the films (Fig. 2). The microstructure of the pure hydrogen free carbon film is shown in Fig. 2(a). Nanocrystalline graphite-clusters were observed, with a dispersion of clusters approximately 5 nm in size. The microstructure of the hydrogen free carbon film with 2.5 at%Ti was also found to consist of a nano-crystalline graphite structure within an amorphous carbon matrix, and grain growth and development of the texture were found to occur. However, no crystalline texture was observed in the microstructure of the nc-C film with 2.5 at% Au. From this result, it can be suggested that Ti concen-

Table 2. Chemical bonding state changes of metal contained carbon films

	Ti doped nc-C					Au doped nc-C			
Doping amount (at%Me)	0	1.2	2.5	5.7	12.9	0	2.5	6.7	18.1
Intensity (Cts)	43749	50441	61156	53524	52863	43749	30162	18651	8619
Main peak position (eV)	284.4	284.4	284.4	285	285.1	284.4	284.4	284.4	284.4



(a)



(b)

Fig. 2. XPS analysis of Me:nc-C films; (a) Ti doped nc-C, (b) Au doped nc-C.

tration leads to the formation of graphitic nanocrystalline clusters in the amorphous carbon matrix and plays the role of a seed for the crystallization of carbon.

3.4. Electrical Properties of Metal Containing nc-C Films

The electrical resistivity of the deposited metal containing nc-C films as a function of the amount

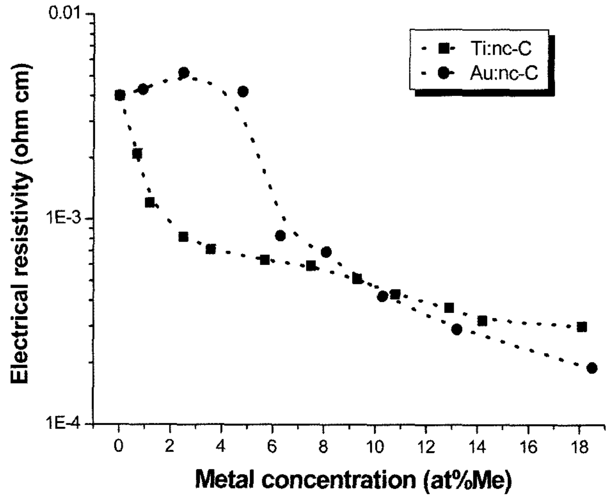
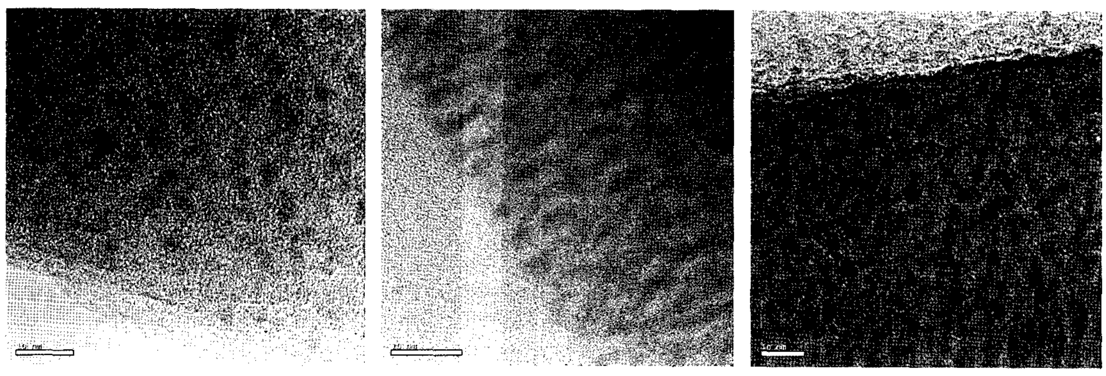


Fig. 4. Electrical resistivity of nc-C films with the variation of elemental doping amount.

elemental concentration is illustrated in Fig. 3. The electrical resistivity of the Ti containing nc-C films decreases rapidly with increasing amount of Ti contained and then decreases gradually, attaining a minimum value of approximately 0.2 mΩ·cm when the Ti concentration reaches 18.0 at%. As shown in the XPS and TEM analysis, this behavior could be ascribed to two competitive mechanisms induced by the increase in the amount of Ti concentration, namely the enhancement of the Ti concentration in the low doping amount region that favors the formation of more graphite-like crystalline columnar structured films (higher sp^2 content), and the accumulation of Ti metallic and TiC compound phases with high conductivity in the carbon matrix at high Ti concentrations, due to the presence of the metal doped carbon. Therefore, in this case, the small amount of Ti atoms in the amorphous carbon matrix plays the role of a 'catalyst of crystallization', while the large amount of Ti atoms contributes to formation of the metallic and compound phase and plays the role of a 'conductor'



(a) (b) (c)

Fig. 3. HRTEM micrographs of Me:nc-C films; (a) pure nc-C, (b) nc-C with 2.5 at%Ti, (c) nc-C with at%Au.

between the nano-grains of the carbon phase.

However, the electrical resistivity of the Au containing nc-C films increases gradually with increasing amount of Au concentration and then decreases rapidly, attaining a minimum value of approximately 0.2 mΩ·cm when the Au concentration reaches 18.2 at%. In this case, it can be suggested that the small amount of Au does not act as a 'catalyst of crystallization' owing to the characteristics of this noble metal, while the formation of an Au metallic phase was derived to the high conductivity of the carbon film at high Au concentrations.

4. Conclusions

Hydrogen free nanostructured carbon films were deposited with various materials concentration contents. The microstructure of the nc-C film with 2.5 at%Ti was found to consist of a crystalline columnar structure, while no crystalline texture was observed in the microstructure of the nc-C film with 2.5 at%Au. Moreover, the electrical resistivity of the Ti concentration nc-C films decreases rapidly as the concentration of Ti is increased up to approximately 3 at%Ti, while that of the Au contained nc-C films increases gradually as the Au containing is increased up to about 3 at%Au. Therefore, Ti contained in nc-C films promotes the crystallization and grain growth of the graphite in the amorphous matrix and enhances the electrical conductivity, while concentration of Au plays only a negative role from the electrical point of view.

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