

## **NANO NI DOT EFFECT ON THE STRUCTURE OF TETRAHEDRAL AMORPHOUS CARBON FILMS**

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### **ABSTRACT**

Nano-scale manipulation of thin film structure has attracted much attention, owing to their possibilities to obtain novel properties associated with the nano-scale microstructure. A great effort is also focusing on the nano-scale manipulation of tetrahedral amorphous carbon (ta-C) films. Multilayer structures composed of ta-C films of different properties are the most widely investigated structure. In the present work, we demonstrated that nano-sized graphitic columns embedded in hard amorphous ta-C matrix could be prepared by using nano-sized Ni dots on the substrate surface. The Ni dots were prepared by annealing Ni thin film of thickness ranging from 3 to 13 nm. The ta-C film was then deposited by filtered vacuum arc process. Microstructure analysis and electrical resistivity measurement showed that nano-scale columns of highly conducting graphitic phase grew at the Ni dots. Size of Ni dot has significant effects on the nano-scale structure evolution, and thus mechanical and electrical properties. The growth of the graphitic phase was discussed in terms of the catalyst effect of Ni for the transformation of carbon materials into stable graphitic phase.

**Keywords:** nano-scale structural manipulation, tetrahedral amorphous carbon, filtered vacuum arc process, Nano-sized Ni dots, catalyst effect

### **INTRODUCTION**

Novel properties associated with nano-structures have been widely reported (ref.1). For example, nano-sized powder materials, nano-composite, or nano-scale multilayer thin films frequently exhibit novel properties that cannot be implemented in the materials of conventional microstructures. A great effort is also focusing on the nano-scale manipulation of tetrahedral amorphous carbon (ta-C) films. Although ta-C film has a unique combination of high hardness, chemical stability and optical transparency, high residual compressive stress and poor adhesion has limited their applications (ref.2). Nano-composite films or nano-scale multilayer structures of the films of different properties is being widely investigated to resolve these drawbacks (refs.3 to 4). Search for novel properties of nano-structured ta-C film would also be the motivation of these investigations.

In the presented work, we developed a method to obtain nano-scale structural manipulation of ta-C film deposited by filtered vacuum arc process. By incorporating nano-sized Ni dots on the substrate surface, we could obtain highly conducting graphitic phase grown from the Ni dots to the surface of ta-C film. Since the catalyst effect of Ni for the transform to more stable graphitic phase, this method resulted in nano-composite materials in lateral dimension, i.e. nano-sized graphitic columns embedded in hard amorphous ta-C matrix. The reduction of mechanical properties and electrical resistivity with increasing size of the Ni dots could be understood in the viewpoint of the local increase of  $sp^2$  bonds in hard ta-C matrix.

### **EXPERIMENTAL PROCEDURE**

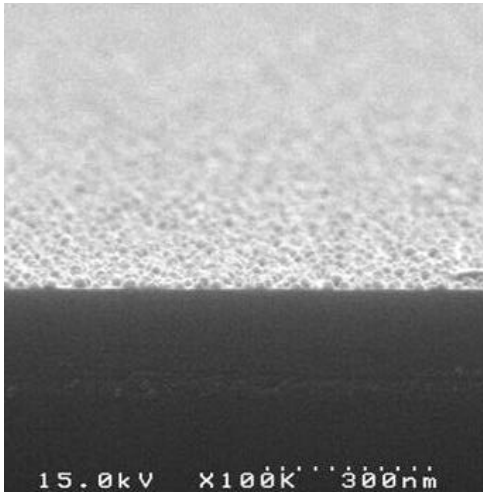


Figure 1. SEM microstructure of Ni dots formed by annealing of sputter deposited Ni film of thickness 3.4 nm

The structure of the film was analyzed by employing transmission electron microscopy (TEM). The electrical resistivity of the film was measured by a four-point probe method. The residual stress of the film was obtained from curvature of film/substrate composite using Stoney equation (ref.5). Nanoindentation in continuous stiffness measurement (CSM) mode was used to characterize the hardness and the plane strain modulus of the film. Atomic-bond structure was analyzed by using a Raman spectroscopy. Raman spectra were obtained by a triple-Raman spectroscope in the range from 800 to 2000  $\text{cm}^{-1}$ , using an Ar ion laser of wavelength 514.5 nm.

Nano-sized Ni dots on Si substrate were prepared by annealing Ni thin films of thickness ranging from 3 to 13 nm. The Ni thin film was deposited on the 600- $\mu\text{m}$ -thick Si (100) wafers by DC magnetron sputtering method. In order to change the deposited Ni film to nano dots, the specimen was annealed in a rapid thermal process (RTP) at 800°C for 15 min in hydrogen environment. Hydrogen pressure during the annealing was kept at 1 Torr by adjusting the flow rate of hydrogen. Figure 1 is typical SEM microstructure of Ni dots obtained by the present annealing process. Ni dots of diameter ranging from 15 to 90 nm were uniformly distributed on the substrate. The average size of nano Ni dots monotonically increased with the thickness of the Ni film.

After Ni dot pretreatment, 100-nm-thick ta-C films were deposited by using filtered vacuum arc process. Details of the deposition equipment have been described elsewhere (ref.3). Prior to deposition, the substrate was pre-cleaned by carbon arc plasma beam mixed with Ar ions at the negative bias voltage of -800 V. The Si (100) strips with thickness of 100 $\pm$ 5  $\mu\text{m}$ , with and without Ni dot, were also used as the substrate to measure the residual stress of the

## RESULTS AND DISCUSSION

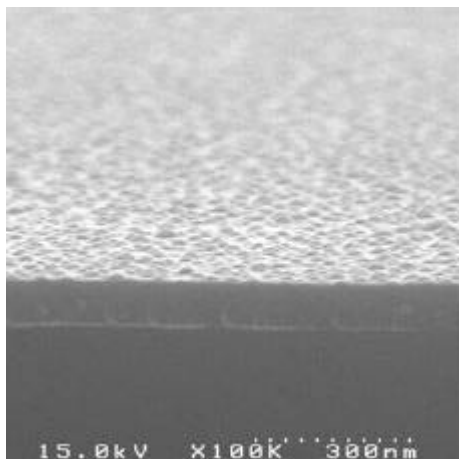


Figure 2. SEM microstructure of ta-C film deposited on the substrate of Fig. 1.

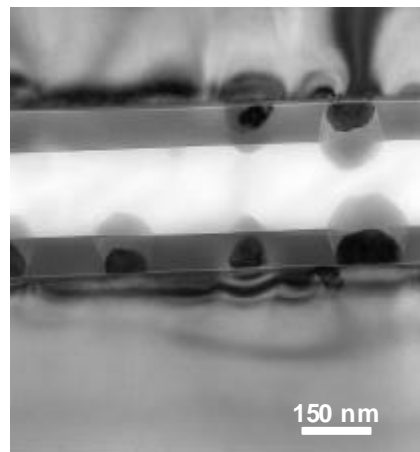


Figure 3. TEM cross-section of the ta-C film deposited on the substrate of Fig. 1.

Figure 2 shows the typical SEM microstructure of ta-C coated surface on the substrate shown in Fig. 1. Composition of the film analyzed by Auger spectroscopy was pure carbon without any impurities of Ni or Si on the film surface. The morphology of the nano-sized Ni dots on the substrate remained on the deposited surface. The rms roughness of the surface measured by an atomic force microscope increased from 2.07 to 25.1 nm as the thickness of the Ni film increased from 3.4 to 13.1 nm. Figure 3 shows TEM cross-section of the ta-C film with nano-sized Ni dot on the substrate. The microstructure showed that a nano-scale second phase was grown on the nano-sized Ni dots. The second phase could be clearly distinguishable not only from Ni dots but from the amorphous carbon matrix. The size of the second phase is closely related with those of Ni dots. In the case of the smallest Ni dots prepared from the thinnest Ni film of 3.4 nm, the second phase was so small that could not reach to the film surface. However, the size of second phase increased as that of Ni dots increased.

The content of the second phase is proportional to the size of Ni dots that is in turn proportional to the thickness of Ni film. Therefore, the properties of the film were analyzed as a function of thickness of Ni film to understand the characteristics of the second phase. Figure 4 shows the dependence of electrical resistivity and the Raman spectra on the thickness of Ni films. The resistivity gradually decreased until thickness of deposited Ni film was 3.4 nm. However, the resistivity dropped by approximately 5 orders of magnitude when the thickness was larger than 3.4 nm. This behavior is in parallel with the structural evolution that the growth of the second phase reached to the surface only when the thickness of Ni film is larger than 3.4 nm. Hence, the present observation showing that the conducting path was formed in the insulating ta-C matrix as the size of Ni dot increased, would suggest that the second phase grown from the Ni dots is highly conducting.

Raman spectroscopy has been extensively used to study the structural variation in amorphous carbon materials such as hydrogenated amorphous carbon (a-C:H) or tetrahedral amorphous carbon (ta-C) films in addition to diamond or graphite (ref.6). Raman spectroscopy can reveal two aspects of the film properties. Intensity of the peak near  $980\text{ cm}^{-1}$ , the second order Raman excitation of Si, is a measure of the optical transparency of the film. Raman spectra of Fig. 4 (b) show that the intensity significantly decreased when the thickness of Ni was larger than 3.4 nm, which implies that the optical transparency of the film was degraded with increasing content of the second phase. On the other hand, intensity of the peak at  $1550\text{ cm}^{-1}$  (also referred to as G peak) increased as the thickness of Ni film increased. It is well known that the G peak originates from  $E_{2g}$  phonons among the zone center modes of graphite sheet (ref.7). Since the film thickness was kept at 100 nm in all cases, this result suggests the increase of  $sp^2$  bonds in ta-C matrix. Combined with electrical resistivity measurement, these observations show that the second phase grown at the Ni dots is  $sp^2$ -rich graphitic phase which is electrically conducting and optically less transparent.

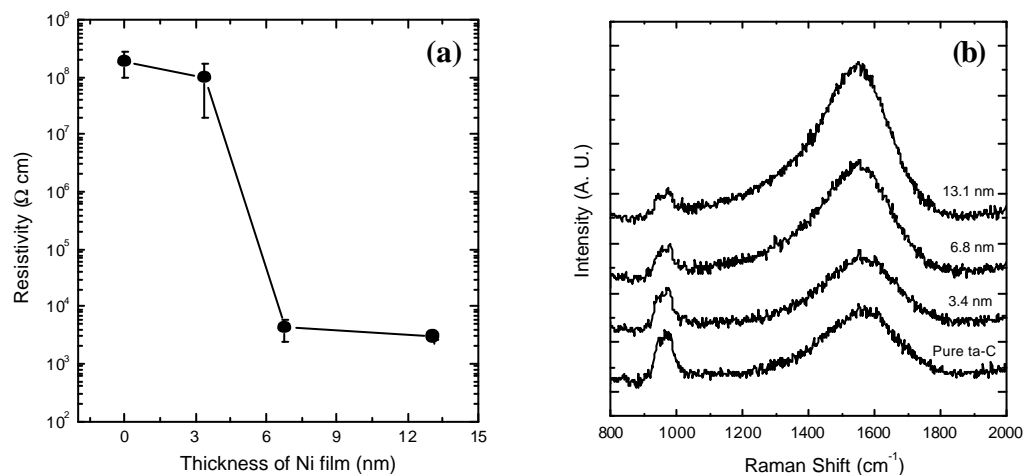


Figure 4. (a) The change of electrical resistivity of the film as the thickness of the Ni film and (b) Raman spectra for various values of thicknesses of the Ni film.

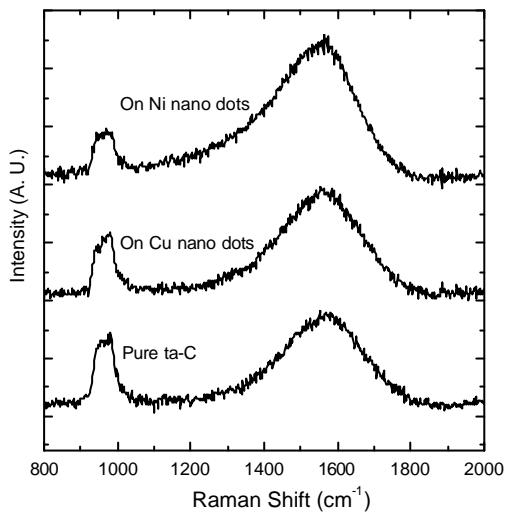


Figure 5. Raman spectra of the film for various cases of metal dots on Si substrate.

## CONCLUSIONS

Nano-scale structural modification in lateral dimension was possible by filtered vacuum arc deposition of carbon using Ni nano dots on the Si substrate. Structural analysis and electrical resistivity measurement revealed that highly conducting graphitic phase was grown on the nano-sized Ni dots, which resulted in the nano-scale conducting phase embedded in amorphous ta-C matrix. The structural manipulation was due to the catalyst effect of Ni for the transformation of carbon to the more stable graphitic phase.

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Fig. 5 shows the Raman spectra when using Cu nano-dots instead of Ni dots. For comparison, Raman spectra of homogeneous pure ta-C film deposited without metal dots and the film with Ni nano dots of the same were also presented. In contrast to the case of using Ni dots, the Raman spectrum was essentially identical to that of pure ta-C film when using Cu nano dots. Transition metals such as Ni, Co are well known to be the catalyst for the transformation of amorphous carbon to more stable graphite. Lamber *et al.* reported that Ni catalyzed effectively the conversion of amorphous carbon to graphitic carbon at temperature as low as 730 °K (ref.8). It can be thus said that the catalyst effect of Ni for enhancing the transformation to stable graphitic phase played a major role for the structural evolution of the present work. Thermal activation for the phase transformation seems to be provided by the high energy ion bombardment on the growing surface or high flux of electrons from the arcplasma.

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