Nanoscale manipulation of tetrahedral amorphous carbon films

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Abstract

The outstanding mechanical, chemical and tribological properties of tetrahedral amorphous carbon (ta-C) films have attracted much attention. For a wide variety of applications, a great effort should be focused on the nanoscale structure control. In the present work, we have adopted a novel technique for nanoscale manipulation of ta-C films; incorporating nano Ni dots at the interface between the ta-C film and the substrate. For Ni dot pretreatment, the Ni thin film was deposited and annealed prior to the ta-C films deposition. TEM and Raman spectrum analysis shows that the nano Ni dots at the interface between the film and the substrate results in nanoscale graphitic phase embedded in hard ta-C matrix. Mechanical and electrical properties were strongly dependent on the changes of the Ni-induced second phase. The reduction of mechanical properties and electrical resistivity with increasing the size of Ni dots could be understood in view of the local increase of sp\textsuperscript{2} bonds in hard ta-C matrix.

Keywords: DLC; ta-C, tetrahedral amorphous carbon; FVA; Ni

1. Introduction

The outstanding mechanical, chemical and tribological properties of tetrahedral amorphous carbon (ta-C) films have attracted much attention. It is well known that these unique properties were due to a high ratio of sp\textsuperscript{2} hybridized carbon bonds in ta-C films [1]. It is achieved by bombarding a high flux of carbon ions of kinetic energy ranging from 10 to 100 eV onto the deposited surface. The mass selected ion beams, pulsed laser ablation and filtered vacuum arc [1–3] are typical processes adopted for this purpose. However, different applications require different structures and morphologies of ta-C films. Therefore, developing a way to control the nanoscale structure of ta-C is prerequisite for a variety of practical applications.

However, transition metal such as Ni, Co has been a well-known catalyst for conversion of amorphous carbon to graphite. Therefore, they are widely used as catalysts for carbon nanotube [4]. Lamber et al. reported that Ni effectively catalyzed the conversion of amorphous carbon to graphitic carbon at temperature as low as 730 K [5].

In the present work, we have adopted a novel technique for nanoscale manipulation of ta-C films; incorporating nano-sized Ni dots at the interface between the ta-C film and the substrate. TEM and Raman spectrum analysis shows that the nano-sized Ni dots results in nanoscale graphitic phase embedded in hard ta-C matrix. The reduction of mechanical properties and electrical resistivity with increasing of the size of Ni dots could be understood in view of the local increase of sp\textsuperscript{2} bonds in hard ta-C matrix.

2. Experimental

For Ni dot pretreatment, the Ni nano thin film was deposited and annealed prior to the ta-C film deposition. Ni was deposited on the 600-\textmu{}m thick Si(100) wafers by the DC magnetron sputtering method. The thickness of the Ni film ranged from 3 to 13 nm. In order to change the deposited Ni film to nano dots, the specimen was annealed in a rapid thermal process (RTP) at 800 °C in a hydrogen environment for 15 min. Hydrogen pressure during the annealing was kept at 1 torr by adjusting the flow rate of hydrogen. Fig. 1 is a 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 size
of nano Ni dots was strongly dependent on the thickness of the Ni film.

After Ni dot pretreatment, 100-nm thick ta-C films were deposited on these specimens and Si wafers by using the filtered vacuum arc system. Details of the deposition equipment have been described elsewhere [6]. Prior to deposition, the substrate was pre-cleaned by using the 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 $\mu$m, with and without Ni dot, were also used as the substrate to measure the residual stress of the film. 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 system. The residual stress of the film was obtained from curvature of film/substrate composite using the Stoney equation [7]. Nanoindentation in continuous stiffness measurement (CSM) mode was used to characterize the hardness and the plane strain modulus of the film. The atomic–bond structure was analyzed by using Raman spectroscopy. Raman spectra were obtained by a triple-Raman spectro-

3. Results and discussion

Fig. 2 shows typical morphologies of ta-C film deposited on the substrate with nano Ni dots shown in Fig. 1. The surface roughness increases with increases in the size of Ni dots, while pure ta-C films retain the initial smoothness ($rms = 0.2$ nm). This means that the surface roughness is mainly due to nano Ni dots. This behavior was also confirmed by an atomic force microscope (AFM) analysis with tapping mode. The AFM studies reveal that the value of $rms$ increases from 2.07 to 25.1 nm when the thickness of the deposited Ni film increases from 3.4 to 13.1 nm.

Fig. 3 is a TEM microstructure and corresponding AFM image of ta-C film on nano Ni dots. It shows the film is composed of nano Ni dots at the interface between ta-C film and the Si substrate, nanoscale second
phase of Ni dots in the amorphous carbon matrix. The most striking feature in the present work is that the second phase, extending from the Ni dot up to the film surface, is distinctly distinguishable not only from the Ni dot but also from the pure ta-C matrix. The size and effect on the flat surface of second phase is closely related with the nano Ni dot size. In the case of the smallest Ni dot size, this is, the thickness of deposited Ni film is 3.4 nm, the second phase is very small and does not reach the surface. However, the second region around the Ni dots increased with increasing the size of Ni dots. Although the crystalline structure of the region is still not known, it is clear that this region is different from the pure ta-C matrix. This will be discussed further in the following paragraphs.

Fig. 4 shows that electrical resistivity varied with the Ni dot size. It is well known that pure ta-C films have the high electrical resistivity as shown in this figure. The resistivity gradually decreases until thickness of deposited Ni film is 3.4 nm. However, the resistivity dropped by approximately 5 orders of magnitude as the Ni film thickness increased up to 6.8 nm and then gradually decreased. As shown in Figs. 2 and 3, surface modulation with second phase was clearly observed since the thickness of deposited Ni film was 6.8 nm. This sudden drop in the resistivity strongly suggests that some conducting path be formed in the insulating ta-C matrix. Furthermore, the resistivity was inversely proportional to the content of the second phase. It can thus be said that the second phase around Ni dots could be an effective conducting region.

Fig. 5 shows the dependence of the residual stress on the size of Ni dots. The residual stress decreased from 6 to 3 GPa as the thickness of deposited Ni film was increased from 0 to 13.1 nm. Hardness and the plane strain modulus of the deposited film are summarized in Fig. 6. The mechanical properties showed the same dependence on the size of Ni dots. The second phase must be softer than the ta-C matrix since the stress and mechanical properties decreased with second phase content. (However, the uncertainties due to the substrate effect should be considered in the nanoindentation meas-
Fig. 7. Raman spectra of deposited films for various Ni dots size. The spectra were shifted upward for ease of comparison.

urements [8]. The substrate effect would cause under-
estimation of hardness in hard film deposited on soft Ni
dots.) The reduction of stress and mechanical properties
would suggest two possibilities for the role of nano Ni
dots. Firstly, the Ni dots may enhance the graphitization
of amorphous carbon around them. In this case, the
changes not only of the mechanical properties, but also
of the resistivity, can be explained. Secondly, Ni dot
itself, softer than the ta-C matrix, may have affected the
mechanical property reduction. In this case, however,
the reduction of electrical resistivity cannot be explained
since the Ni dots were encosed by the ta-C matrix.

Raman spectroscopy is a comparatively simple and
non-destructive analysis tool to characterize the struc-
tural change of carbon materials. It has been thus
tensively used to study the structural variation in
amorphous carbon materials such as hydrogenated amor-
phous carbon (a-C:H) or tetrahedral amorphous carbon
(ta-C) films in addition to diamond or graphite [9–11].
Fig. 7 shows the Raman spectra of deposited films.
Because of the higher sp³ content in ta-C films, the
Raman peak of carbon in ta-C films is generally much
smaller than that from amorphous hydrogenated carbon
(a-C:H) films. Furthermore, the D-peak shoulder is
much weaker in ta-C films, resulting in a more sym-
metric carbon Raman peak. The peak 960 cm⁻¹ is the
second-order peak of the Si substrate. Hence, the inten-
sity of the Si peak is a measure of the optical transpar-
ency of the films. As shown in Fig. 7, the shapes of the
Raman spectra were essentially similar. It means that all
of the films have mainly ta-C matrix. However, the pure
ta-C film shows the higher Si second-order peak and
the lower carbon peak compared to those of the film
deposited on the substrate with nano Ni dots. Further-
more, the intensity of carbon peak increased with the
size of Ni dots. It should be noted that the film thickness
is identical for all specimens in Fig. 7. Therefore, the
increase in the carbon peak suggests the local increase of sp² bonds in ta-C matrix, which, in turn, is
closely related to the Ni dot size. Thus, it can be said
that the second phase around Ni dots shown in Fig. 3
is a sp²-rich region. Hence, the reduction in electrical
resistivity and residual stress observed in Figs. 4 and 5
could be understood in terms of the local increase of
sp² bonds.

In summary, the observed behavior could be under-
stood in terms of the changes in the atomic bond
structure caused by nano Ni dots. The apparent effect
of nano Ni dots was the formation of the second phase
only around Ni dots, which is distinctly distinguishable
not only from the Ni dot but also from the pure ta-C
matrix.

Filtered vacuum arc process can provide sufficient
energy (approx. 25 eV in the present work) to heat
locally amorphous carbon on the Ni surface. For exam-
ple, Weissmantel et al. reported that for carbon with 100
eV a region with a radius \( r_0 \) of 0.75 nm is heated at
least to the melting point \( T_m = 3823 \) K based on the
thermal spike model [12]. However, electron microscop-
ic studies revealed that amorphous carbon transform to
graphite already at relatively low temperatures (e.g.
above 730 K) when amorphous carbon is in contact
with Ni [5]. These support the previous arguments that
the second phase is the sp²-rich region. Therefore,
experimental results could be understood in the point
the local increase of sp² bonds in the hard ta-C matrix.
When the Ni dot size is small (the thickness of Ni film
was 3.4 nm), the degree of second phase formation is
small. The stress and mechanical properties decreased
in proportion to sp² content while the change in the
electrical resistivity was not significant. However, when
the Ni dot size increased (the thickness of Ni film
exceeds 6.8 nm), the content of the Ni-induced second
phase increased. Furthermore, sp²-rich region extended
from Ni dot up to the film surface. This structural
change resulted in not only the reduction of stress and
mechanical properties but also the sudden drop in the
resistivity, since the second phase could provide an
effective conducting path.

4. Conclusions

Ni dot pretreatment and filtered vacuum arc process
was used for nanoscale manipulation of ta-C films which
have the outstanding mechanical, chemical and tribolog-
ical properties. For nano Ni dot pretreatment, the Ni
thin film was deposited and annealed prior to the ta-C films deposition. The most striking feature in the present work is that the second phase dispersed only around Ni dots is distinctly distinguishable not only from the Ni dot but also from the pure ta-C matrix. The content of the second phase is closely related with nano Ni dot size. It was observed that residual stress and mechanical properties decreased with increasing the size of Ni dots.

Structural analysis and electrical resistivity measurements evidently showed that the second phase could be sp²-rich regions. Furthermore, there is the possibility of the conversion of amorphous carbon to graphite, because Ni could act as a catalyst effect due to the high carbon ion energy provided by FVA.

The reduction of mechanical properties and electrical resistivity with increasing of the size of Ni dots could be understood in view of the local increase of sp² bonds in hard ta-C matrix. This structure modulated ta-C films in which sp²-rich regions only around nano Ni dots dispersed in sp³-rich matrix would have a potential for a wide variety of applications.

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References