Modification of physical properties of chemical vapor deposited nanostructure diamond by argon-hydrogen plasma surface treatment

© Y. Hayashi, D. Mori, T. Soga, T. Jimbo

Department of Environmental Technology and Urban Planning, Nagoya Institute of Technology, Nagoya 466-8555, Japan

E-mail: hayashi.yasuhiko@nitech.ac.jp

Nanostructure diamond (NSD) film with the hardness as high as 70 GPa and the average surface roughness of 10 nm has been synthesized by the two-step negative substrate bias method combined with post-growth Ar–H_2 plasma irradiation. The Ar–H_2 plasma irradiation has been confirmed to improve the uniformity of grain size and shape, and increase the hardness of the NSD film. This work was partly supported by the Research Foundation for the Electrotechnology of Chubu (REFEC), the Daiko Foundation and the NITECH 21st Century COE Program „World Ceramics Center for Environmental Harmony“.

1. Introduction

Compared with the polycrystalline diamond film, the nanostructure diamond (NSD) film is very attractive for many industrial applications due to their unique bulk and surface properties such as the high optical band gap, high hardness, high thermal conductivity and low electrical conductivity by doping [1–3]. The smoother surface and the wide band gap provide the opportunity to act as ideal transparent protective films on optical components [4]. Polishing of polycrystalline diamond with either chemical or mechanical methods seems to be impractical due to its extreme hardness and chemical inertness. Thus, the efficient approaches have to be exploited to grow the transparent diamond film through reducing micrometer scale diamond grain down to nanometer scale [5]. Moreover, the possibilities of microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) devices by using ultra-nanocrystalline diamond (UNCD) have been explored by Gruen et al. [6].

Nanocrystalline diamond has been successfully grown with a microwave plasma enhanced chemical vapor deposition (MPECVD) using either CH_4–H_2 or Ar–CH_4 gas mixtures and fullerene-argon mixture as a precursors [1,7–9]. Morphology of the diamond film depends on reactant gases, their mixing ratios, negative substrate bias and the substrate temperature. CVD diamond films are most commonly grown using low partial pressures of CH_4 in H_2. As the partial pressure of CH_4 increases, the crystalline morphology disappears, and diamond-like carbon (DLC), which contain both low quality and graphite-like phase is formed. In recent years, it has been found that growing at specific conditions between these two extremes can yield high quality diamond films containing small NSD in disordered graphite.

It is well known that the grain size is one the important factor influencing on properties of NSD film. However, the nucleation mechanism and properties of NSD film remain poorly understood, because of difficulty in locating and controlling nucleation sites. In this report, we investigate the properties of NSD film deposited by a MPECVD with-step negative substrate bias and post-growth H_2–Ar plasma irradiation. The two-step substrate bias (SB) process, consisting of a high negative SB at bias-enhanced nucleation (BEN) for a short time followed by a lower negative SB at bias-enhanced growth (BEG), enables to control hydrogen ion energy in the plasma which expected to play a dominant role to surface modification and hardness of the NSD film [9,10]. We will discuss the effect of the substrate temperature at the BEG step and H_2–Ar plasma irradiation after NSD deposition.

2. Experimental

The NSD films were deposited in a 2.45 GHz MPECVD system with a two-step negative substrate bias to reduce the residual stress and the surface roughness. The mirror-polished Si(100) substrates, pretreated in an aqueous solution of HF ($HF:H_2O = 1:1$ by volume) to remove the oxide, were set on a molybdenum (Mo) holder. Then they were cleaned with H_2 plasma for 20 min at 900°C. The CH_4 concentration, microwave power (MP), and total pressure were maintained at 5%, 1000 W, and 30 Torr, respectively. The growth time at BEN and BEG steps were 5 and 60 min, respectively. The substrate temperature was varied from 400 to 800°C while keeping the substrate bias at BEN of −300 V. After deposition, NSD films were treated by the mixture of Ar–H_2 plasma irradiation with different $Ar/(H_2+Ar)$ ratios at MP of 1000 W for 30 min.

The surface morphological features of nucleation stage in NSD films were examined using a Seiko Instruments SPI-3800N CAFM system with a Pt probe in a vacuum of 10^{-7} Torr. Structural characterizations of the films were carried out by Raman spectra in the back-scattering geometry using the 514.5 nm line of an Ar^+ ion laser at room temperature in the spectral range from 900 to 1800 cm^{-1} with a resolution of 1.0 cm^{-1}. The crystallographic structure and crystallinity of NSD films were investigated by X-ray diffraction (XRD) with quite shallow incident X-ray angle using Cu K_α radiation. Hardness of the films was measured by a nanoimdentor (UMIS-200) using a Berkovich diamond pyramid. The deposition rate was around 600–1800 nm/h and, in order to minimize the substrate effect on the

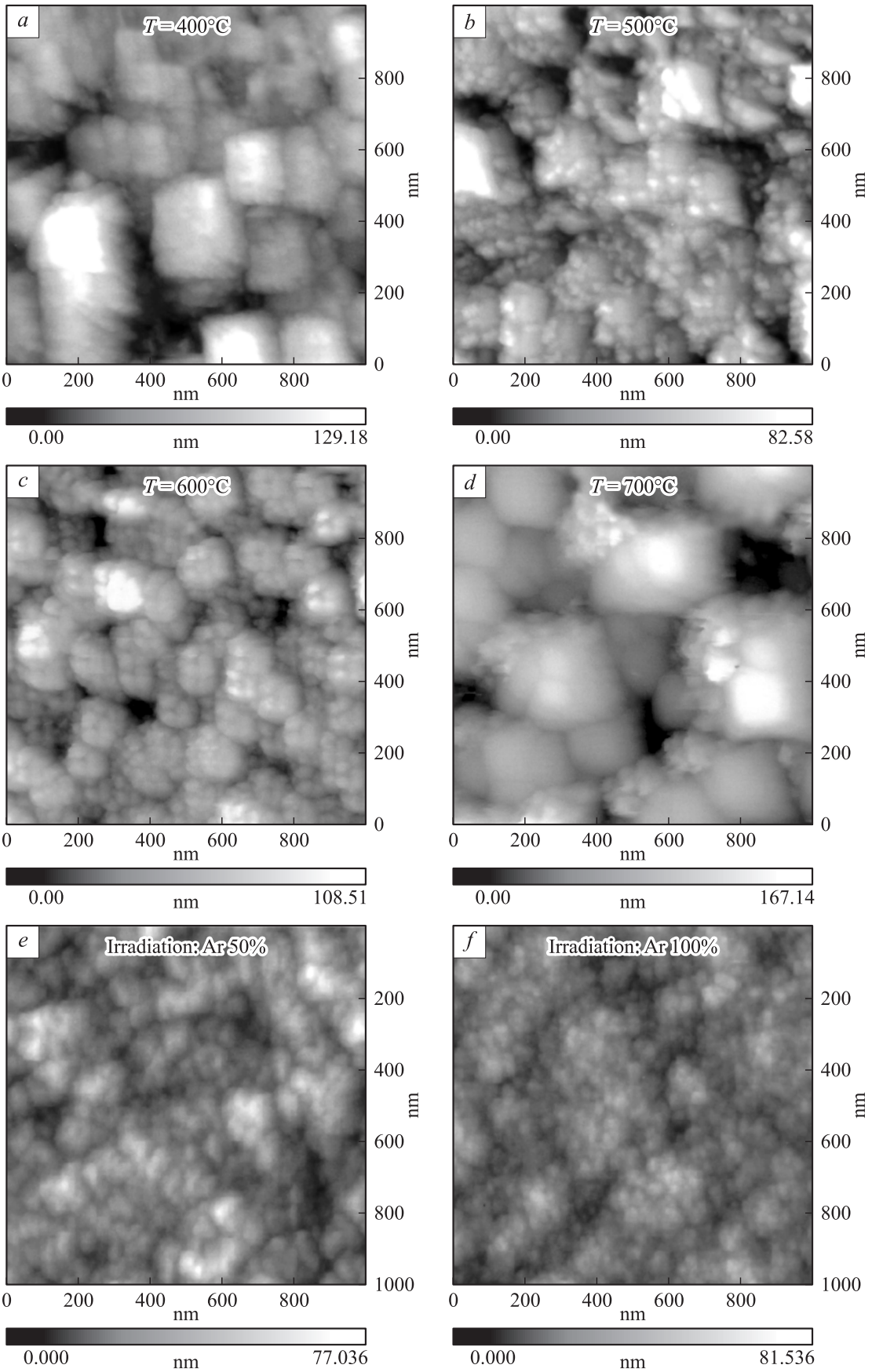

Figure 1. The CAFM surface morphologies of the NSD films deposited at 400 (*a*), 500 (*b*), 600 (*c*) and 700°C (*d*) and the NSD films irradiated by Ar–H_2 plasma with Ar concentrations of 50 (*e*) and 100% (*f*) scanned in a $1 \times 1\,\mu m^2$.

hardness measurements, maximum loading force does not exceed 10 mN. Therefore, the indentation depth was kept within the critical depth (maximum penetration depth should not exceed 10% of the film) beyond which there would be sever effect in the hardness measurement of the film from the substrate. Both the UMIS and indenter tip were calibrated using a fused silica standard of known material properties.

3. Results and discussion

We first investigated in detail the surface morphology of NSD films. CAFM shows clear morphological change with variation of the substrate temperature, as shown in Figs. 1, *a*—*d*. For the substrate temperature of 600°C, the large cauliflower-like clusters of 100–130 nm in diameter, which are composed of many 30–50 nm in diameter small and uniform grains, were obtained, as shown in Fig. 1, *c*. The morphology of cluster changes from a cauliflower-like to a columnar above 700°C. The size and shape of clusters strongly depend on the substrate temperature. We clearly find, as shown in Fig. 1, *a*, the high uniformity of the trapezoidal (columnar) shape clusters composed of small grains, 200 nm square and 100 nm high, which are connected with each other and enhance the alignment of nuclei below 500°C. In other words, a high density (or coverage) of {100}-oriented, textured grains has been obtained. For a substrate tempetature above 700°C, some portion of the small grains coalesces together to form crystallites, while the boundary of crystallite contains individual grains. The current value of the conducting region increased with increase in the substrate temperature. The comparison of CAFM current image of NSD films deposited between 400 and 700°C revealed that the conductive difference is at least a magnitude of one order. Thus, the surface graphitization of the depositing NSD film might be produced from films deposited above 700°C. The average roughness (Ra) and root mean square (RMS) roughness, as shown in the inset in Fig. 2, *a*, decreased from 9.8 nm and 12.5 nm to 9.0 and 11.3 nm, respectively, as the substrate temperature is increased from 400 to 500°C. However, both Ra and RMS again increase as the substrate temperature in increased above 600°C. Figs. 1, *e* and *f* show the typical surface morphologies of NSD films, deposited at 500°C as shown in Fig. 1, *b*, irradiated by Ar–H_2 plasma with Ar concentrations of 50% and 100%, respectively. It is clear that the significant morphological change was observed by Ar–H_2 plasma irradiation compared to the cauliflower-like surface morphology of the NSD film deposited at 500°C, as shown in Fig. 1, *b*. Moreover, both Ra and RMS of CAFM, which are shown in the inset in Fig. 2, *b*, were almost unchanged and the relation between surface roughness and Ar concentration could not be established. Both Ra and RMS slightly decrease and the density of small clusters increases by introduction of the Ar–H_2 plasma irradiation after NSD deposition. The uniformity of size and shape of grains is improved by the Ar–H_2 plasma irradiation. And therefore, the surface of NSD film turns out to be smoother. We also observed a significant difference in grain boundary from the NSD film, not shown here, irradiated by only H_2 plasma (Ar = 0). The surface roughness of CAFM increased with increase in H_2 plasma exposure time.

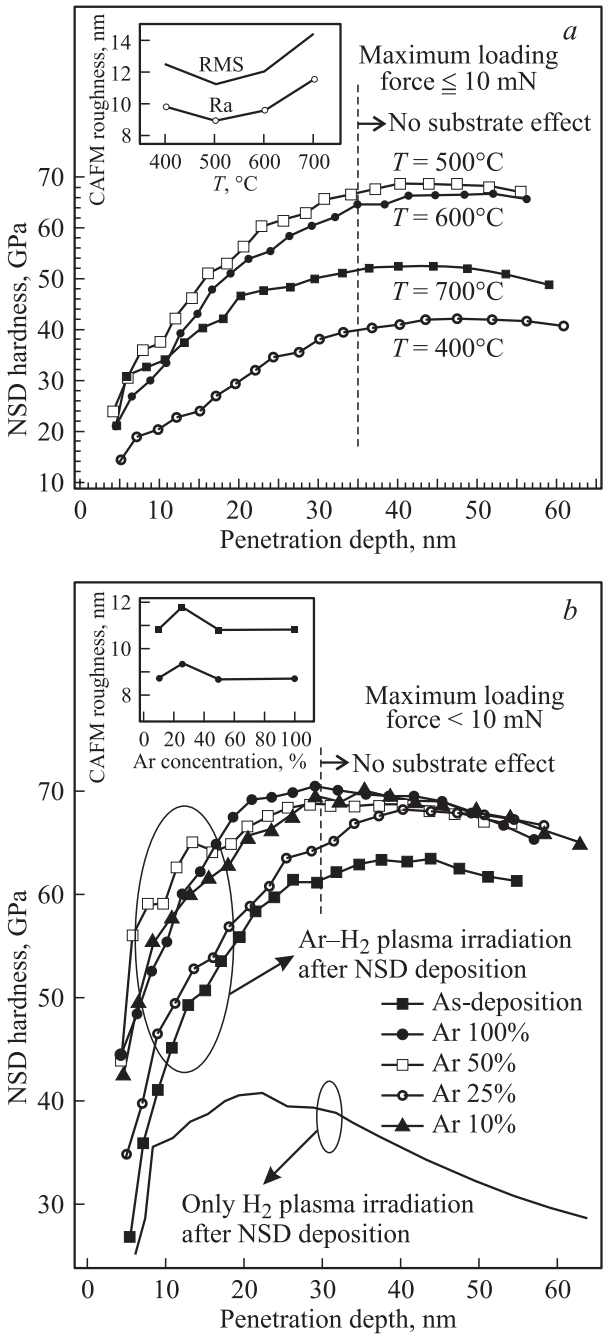

Figure 2. The hardness-penetration curves of NSD films (*a*) with different substrate temperature and (*b*) irradiates by Ar–H_2 plasma with different Ar concentrations indented to maximun load of 10 mN. The insets in (*a*) and (*b*) show the CAFM roughness of NSD films as a function of the substrate temperature and Ar concentration, respectively.

Fig. 2, *a* shows the hardness-penetration curves of NSD films with different substrate temperatures indentes to the maximum load of 10 mN. The inset in Fig. 2, *a* illustrates the CAFM roughness of NSD films as a function of the substrate temperature. The data show that the hardness of the NSD film is constant over the 35–60 nm penetration depth range and there is almost no influence of the substrate on the measured hardness values. The hardness increases with increase in the temperature up to around 600°C and decreases with further increase in temperature. The maximum hardness of 68 GPa was obtained from the NSD film deposited at 500°C. The hardest NSD film was obtained where the CAFM values of Ra and RMS were minimum. Fig. 2, *b* shows the hardness-penetration curves of the Ar–H_2 plasma irradiated NSD films with different Ar concentration. The inset in Fig. 2, *b* illustrates the CAFM roughness of NSD films as a function of Ar concentration during Ar–H_2 plasma irradiation after NSD deposition. The as-grown NSD film was deposited at the substrate temperature of 600°C and the initial hardness of NSD film was 60 GPa. It is clear that the film hardness increased from 60 to 70 GPa with increase in Ar concentration during Ar–H_2 plasma irradiation. Here, it is worth to note that the hardness of the film irradiated by only H_2 plasma (40 GPa) decreases significantly as compared to that of the non-irradiated film (60 GPa). This result indicates the importance of little or no H_2 during Ar–H_2 plasma irradiation.

Visible Raman data obtained for NSD films show similar line shapes which composed of four main peaks located at 1140, 1350 (*D*-peak), 1460 and 1580 cm^{-1} (*G*-peak). Both *G* and *D* peaks are attributed to sp^2-bonded carbon. The peak at 1140 cm^{-1} has been attributed to nanocrystalline diamond, however, the interpretation of this peak is still not fully resolved. In comparison with the non-irradiated film, although the peak at 1460 cm^{-1} decreases, the Ar–H_2 plasma irradiation of NSD films affects no significant change in overall Raman features. On the other hand, however, both 1140 and 1460 cm^{-1} peaks were disappeared while *G* and *D* peaks still remained from the NSD film subjected to only hydrogen plasma (Ar = 0).

XRD results reveal that out NSD films mostly consisted of cubic diamond (111). Although, both diamond (111) and diamond (220) are reported from the NSD film deposited by continuous BEN method there was no signal at $2\theta = 75°$ of sugnature of diamond (220) in our films. It should be noted that the NSD film composed of highly (111)-oriented diamond which was achieved by using two-step negative bias method. XRD spectra of films irradiated by Ar–H_2 plasma with different Ar concentration show that the absolute intensity of diamond (111) is weaker than those of non-irradiated films, and the diamond (220) observed in all irradiated films. Thus, the NSD film gradually changes from (111)-oriented diamond to a randomly oriented phase by the Ar$-H_2$ plasma irradiation.

4. Conclusion

In conclusion, the NSD films composed of (111)-oriented diamond nanocrystals were grown by the two-step negative substrate bias method. The maximum hardness of as high as 70 GPa with the smallest Ra ans RMS of CAFM is obtained at substrate temperature of 500°C. The hardness of film increased by post-growth Ar–H_2 irradiation due to improvement of uniformity of smaller grain size and an smooth surface of NSD film. The hardness and flatness of film irradiated by only H_2 plasma, however, decreased in comparison with non-irradiated film. Thus, we confirm that the introduction of the Ar–H_2 plasma after NSD deposition is effective to increase hardness of films. Our results demonstrated that hard NSD films can be produced from the Ar–H_2 plasma irradiation after NSD deposition with little or no H_2 using MPECVD.

References

[1] S. Jiao, A. Sumant, M.A. Kirk, D.M. Gruen, A.R. Krauss, O. Auciello. J. Appl. Phys. **90**, 118 (2001).
[2] J. Philip, P. Hess, T. Feygelson, S. Chattopadhyay, K.H. Chen, L.C. Chen. J. Appl. Phys. **93**, 2164 (2001).
[3] S. Bhattacharyya, O. Auciello, J. Birrell, J.A. Carlisle, L.A. Curtiss, A.N. Goyette, D.M. Gruen, A.R. Krauss, J. Schlueter, A. Sumant, P. Zapol. Appl. Phys. Lett. **79**, 1441 (2001).
[4] K. Chakrabarti, R. Chakrabarti, K.K. Chattopadhyay, S. Chaudhrui, A.K. Pal. Diamond Relat. Mater. **7**, 845 (1998).
[5] L.C. Chen, P.D. Kichanbare, K.H. Chen, J.-J. Wu, J.R. Yang, S.T. Lin. J. Appl. Phys. **89**, 753 (2001).
[6] D. Gruen. Annu. Rev. Mater. Sci. **29**, 211 (1999).
[7] D.M. Gruen, S. Liu, A.R. Krauss, X. Pan. J. Appl. Phys. **75**, 1758 (1994).
[8] R. Csencsits, D.R. Gruen, A.R. Krauss, C. Zuiker. Mater. Res. Soc. Symp. Proc. **403**, 291 (1996).
[9] C.Z. Gu, X. Jiang. J. Appl. Phys. **88**, 1788 (2000).
[10] Y. Hayashi, Y. Matsushita, T. Soga, M. Umeno, T. Jimbo. J. Appl. Phys. **91**, 9752 (2002).