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Effect of XeF laser treatment on structure of nanocrystalline diamond films

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ABSTRACT

Nanocrystalline diamond (NCD) films were deposited on Si substrates by microwave plasma-enhanced chemical vapor deposition (MPECVD) using methane/hydrogen/oxygen (30/169/0.2 sccm) as process gases. Subsequently a thin (0.33 μm) and a thick (1.01 μm) NCD films were irradiated with XeF excimer laser ($\lambda = 351$ nm) with 300 and 600 mJ cm^{-2} of energy densities in air. The NCD films became rougher after laser irradiations. Fraction of graphitic clusters decreased but oxygen content increased in the thin NCD film after laser irradiation. Opposite phenomena were observed for the thick NCD films. Effect of laser irradiation to oxygenation and graphitization of NCD films was correlated with structural properties of free surface and grain boundaries of the thin and thick NCD films.

1. Introduction

Morphology and chemical structure of diamond surface are of interest due to their effects on electric [1,2], electrochemical [3,4] and biological properties [5–7] of diamond films. Diamond surface has been modified by post treatments utilizing various techniques such as wet treatment in a hot acid [8], plasma etching [9,10], heat treatment [11–13], ion bombardment [14–16] and laser irradiation [17–27]. Diamond surface is usually terminated by hydrogen or oxygen. Annealing H- and O-terminated diamond surfaces in vacuum at high temperatures have generated a clean diamond surface or a sp^2 layer-covered diamond surface [11]. Annealing nanocrystalline diamond (NCD) in air or oxygen induced oxidation below 500 °C and etching at higher temperatures [12,13]. About 14 at.% of oxygen could incorporate in NCD by annealing in air [12]. Bombarding NCD with low energy ion beams has caused etching and graphitization of diamond surface [14]. Surface roughness of the NCD could be reduced from 2.5 nm to 1.7 nm. Bombarding diamond with high energy ions has implanted dopants in subsurface and induced damage on surface of diamond [15,16]. Chemisorption of the damaged NCD surface generated an oxygen-containing layer with 19.7 at.% of oxygen upon exposure in air [15]. Annealing ion-implanted diamond under vacuum caused graphitization of the damaged surface [16]. Surface oxidation of diamond has been manipulated by ozone [28] and UV [29,30] treatments. The achievable oxygen concentrations were 44 at.% for ozone treatment and 8.2 at.% for UV treatment, respectively. Laser treatments have been employed to smooth rough polycrystalline diamond [17,18], generate patterns [19–21] and modify diamond structures [22–27]. Irradiating polycrystalline diamond by laser beam at low incidence angle above the ablation threshold could reduce roughness to less than 40 nm [17]. Thin graphitized layer and glassy carbon have formed on diamond surface after laser ablation in air and in various gases [17–20]. A clean diamond surface without graphitic layer could remain after laser ablation of diamond in oxygen [18] or liquid media [19]. Significant amount of oxygen could incorporate at surface (45 at.%) and subsurface (15 at.%) of NCD film after laser treatment in nitrogen-containing environment [27]. Laser wavelength, pulse frequency and energy have been found to influence structure change of diamond surface by laser irradiation. A smooth or irregular morphology has been generated by irradiating diamond with UV or IR laser [22]. Laser induced graphitization propagated vertically under nanosecond or longer pulse but took place layer by layer under femtosecond pulse, leaving graphitic surface and diamond surface after ablation, respectively [23]. Annealing or graphitization has occurred by irradiating diamond with laser at energies below or above graphitization threshold [24,25]. On the other hand, a diamond-like phase has been converted from graphite by an excimer laser irradiation above ablation threshold [26]. Accordingly, laser treatment is capable to reduce roughness of diamond to tens of nanometers and modify diamond surface with different carbon structures and oxygen contents. Besides, laser treatment has an advantage of operating in versatile environments such as vacuum, air, various gases, and liquid media.

In our current work, effects of XeF laser irradiation to structures of nanocrystalline diamond (NCD) films are studied. Structures and surface compositions of NCD films of different thicknesses changed

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with laser energies. These changes were correlated with different oxygenation phenomena on diamond surface and grain boundaries [31].

2. Experimental details

Prior to NCD deposition, p-type Si(100) substrates were treated to enhance diamond nucleation [20]. Two NCD films were grown on the Si substrates placed on a molybdenum holder in a microwave plasma-enhanced chemical vapor deposition (MPECVD) system in a mixture of methane/hydrogen/oxygen (30/169/0.2 sccm), at a pressure of 2.66×10^3 Pa (20 Torr), with a power of 1000 W, at a temperature of 600 °C for 3 and 11 h, respectively. A pulsed XeF laser (Lambda Physik, $\lambda = 351$ nm, 25 ns pulse duration) was used to irradiate the NCD films in air, at 300 and 600 mJ/cm^2 of energy densities, respectively.

Morphologies of the NCD films were inspected by scanning electron microscopy (SEM, JEOL JSM-6500F) and atomic force microscopy (AFM, Veeco CP-R). Chemical structures of the NCD films were examined by Raman spectroscopy (Renishaw 2000) using a He–Cd laser with a wavelength of 325 nm and a beam diameter of about 5 μm at a power of 10 mW. An X-ray photoelectron spectroscopy (XPS, VG ESCA Scientific Theta Probe) using Al K_α (1486.6 eV) radiation was utilized to analyze binding energies of carbon and oxygen on surface of the NCD films.

3. Results and discussion

As-grown diamond films have a cauliflower-like topography, as shown in SEM images in Fig. 1(a) and (b) and AFM images in Fig. 2(a) and (d). The NCD films grown in the MPECVD system for 3 and 11 h have thicknesses of about 0.33 and 1.01 μm, respectively. The thin NCD film has smaller grains than the thick NCD film has. The NCD films have similar cauliflower-like topography after being irradiated with laser shots. Fig. 2 shows AFM images of the NCD films before and after being shot with 300 and 600 mJ/cm^2 of XeF laser. Roughness and grain size for the NCD films measured from AFM analyses are summarized in Table 1. Roughness and average grain size are 19.7 nm and 231 nm for the as-grown 0.33 μm-thick NCD film, and 22.8 nm and 438 nm for the as-grown 1.01 μm-thick NCD film. Roughness and grain size for the NCD films increase with energy densities of laser irradiation. Therefore, laser irradiation may anneal the NCD films yielding larger grains and rougher surfaces.

Fig. 3(a) and (b) presents UV Raman spectra of the as-grown thin and thick NCD films, exhibiting clear diamond peak at 1332–1334 cm^{-1} and graphitic clusters (G band) at about 1580 cm^{-1}, together with small bumps representing diamond nanocrystals at 1160 cm^{-1} and disordered carbon (D band) at about 1350 cm^{-1} [32]. The result of the Raman spectra indicates that the films are composed of nanocrystalline diamond, diamond microcrystals and carbon clusters. Similar Raman spectra (not shown) were derived from the NCD films after laser irradiations. Area ratios of the Raman peaks of corresponding nanocrystalline diamond (I_{nd}), diamond microcrystals (I_{diam}) and disordered carbon (I_D) to the G band (I_G) for the NCD films are listed in Table 2. The thick NCD film has higher ratios of I_{diam}/I_G and I_{nd}/I_G than the thin NCD film. It indicates that more diamond crystals but less graphitic carbon clusters are present in the as-grown thick NCD film than in the thin NCD film. Ratios of I_{diam}/I_G, I_D/I_G and I_{nd}/I_G for the thin NCD film increase with energy densities of laser, indicating decrease of fraction of graphitic clusters. On the contrary, above peak ratios for the thick NCD film decrease with the increase of energy densities of laser. Therefore, laser treatments generate more graphitic clusters in the thick NCD film.

The C1s XPS spectra of the NCD films are shown Fig. 4. These spectra are decomposed into four components at about (I) 284 eV, (II) 285 eV, (III) 286 and (IV) 289 eV. The peaks (I) and (II) relate to C–C or C–H_x bonds, and peaks (III) and (V) correspond to C–O and COOH, respectively [33–35]. Intensity of the peak (I) of thin NCD film decreases but intensities of peaks (III) and (IV) increase with energy density of laser, as shown in Fig. 4(a)–(c). On the contrary, intensity of peak (I) of the thick diamond film increases but intensities of peaks (III) and (IV) decline with energy density of laser. Oxygen concentration on surface of NCD film, calculated from C1s and O1s (not shown) signals, changes from 12.3% to 24.7% for the thin film, and from 18.7% to 6.5% for the thick film after the NCD films were irradiated with 600 mJ/cm^2 of laser. The laser treatment changed oxygen content in the thin and thick NCD films in different trends. A previous study has indicated that exposure of diamond film in air induced oxygen incorporation to diamond surface and grain boundaries [31]. Oxygenation of carbon proceeded faster in grain boundaries than on surface of diamond. Bonded oxygen was more difficult to remove from grain boundary than from surface of diamond. Here we suggest that laser irradiation simultaneously removed oxygen

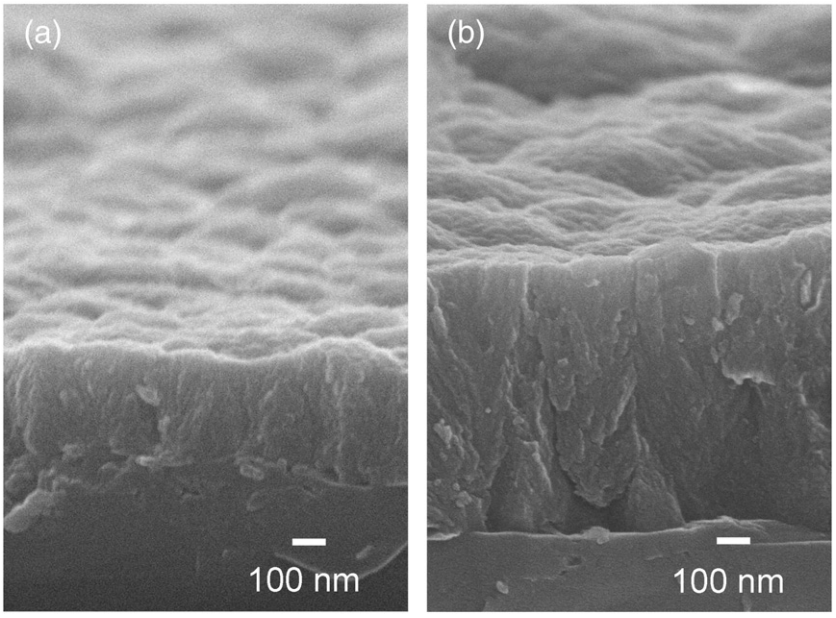

Fig. 1. SEM images for the NCD films deposited in the MPECVD system for (a) 3 h and (b) 11 h.