[논문] 열처리공학회지, 제13권 제5호(2000)
J. of Korean Society for Heat Treatment, *Vol. 13, No. 5, (2000) pp. 318~323*

Planarization of Diamond Films Using KrF Excimer Laser Processing

Dong-Gu Lee
Department of Metallurgical Engineering, Kumoh National University of Technology, Kumi 730-701

KrF 엑사이머 레이저 법을 이용한 다이아몬드 박막의 평탄화

이 동 구
금오공과대학교, 신소재시스템 공학부

Abstract The planarization of rough polycrystalline diamond films synthesized by DC arc discharge plasma jet CVD (chemical vapor deposition) was attempted using KrF excimer laser pulses. The effects of laser incidence angle and reaction gases (ozone and oxygen) on etching rate of diamond were studied. The temperature change of diamond and graphite with different laser fluences was calculated by computer simulation to explain the etching behavior of diamond films. The threshold energy density from the experiment for etching of pure crystalline diamond was about 1.7 J/cm^2 and fairly matched the simulation value. Preferential etching of a particular crystallographic plane was observed through scanning electron microscopy. The etching rate of diamond with ozone was lower than that with oxygen. When the angle of incidence was 80° to the diamond surface normal, the peak-to-valley surface roughness was significantly reduced from 20 μm to 0.5 μm.

(Received July 20, 2000)

Key words: *Diamond Films, Planarization, Excimer Laser, CVD, Ozone, Etching, Ripples*

1. Introduction

CVD diamond has recently received much attention due to its remarkable properties such as extreme hardness, chemical inertness, high wear resistance, high optical transparency from the infrared to the ultraviolet, the highest thermal conductivity at room temperature, wideband gap semiconductor, and field emission properties. Diamond films have great potential in mechanical, optical, and microelectronic applications. However, the CVD diamond films has inherently a high degree of surface roughness, which increases with increasing the thickness of diamond films[1].

Thus, the high roughness of polycrystalline CVD diamond films has become a major obstacle for the industrial applications. The conventional method for planarization of diamond is mechanical polishing with diamond powders. But this technique requires a long time and much labor to achieve planarization of diamond. Many alternative techniques, such as gas ion beam[2,3], polishing with hot plate[4], and laser irradiation at glancing angle[5-7] have been reported. Among these many techniques, planarization of diamond films by laser irradiation is particularly effective due to its fast processing at room temperature without any contacts or size/shape limitations.

A general etching mechanism for diamond using laser pulses has been proposed by Rothschild[8]. This involves a combined photochemical and thermal transformation of the initial diamond crystal to graphite followed by sublimation or chemical reaction of the transformed solid.

The photon energy of the KrF laser (λ=248 nm, E=5.0 eV) is lower than the bandgap energy of diamond (E=5.4 eV). Therefore, diamond can not absorb the incoming laser energy on its surface effectively. However, impurities[9] and defects within or around the diamond crystal grains as well as graphitization of the diamond surface during laser irradiation[8] can absorb more energy, leading to an increase in the etching rate of diamond.

In this experiment, the effects of laser incidence angle and reaction gases (oxygen, ozone) on etching rate, surface morphology, and roughness of diamond films were studied. Also, the surface temperature change with respect to laser fluence was calculated by computer simulation.

2. Experimental

The experimental setup for laser processing for the planarization of diamond films is shown in Fig. 1. The diamond films were irradiated with 20 ns pulses from KrF excimer laser (QUESTEK 2000 series) at a repetition rate of 20 Hz with fluences of 1-4 J/cm^2. The size of the rectangular beam spot was 2 mm × 1 mm when the beam is projected normal to the sample surface. Angle of laser incident (θ) is defined as an angle between laser beam and the surface normal of samples. Laser irradiation of the diamond surface occurred at θ° inside a vacuum chamber at a pressure of 100 torr. Since source gases were directly blown onto the diamond film surface at close distance, we might neglect the pressure effects of chamber during laser processing. The samples mounted on a stage were sometimes given rotation during laser processing.

Thick free-standing diamond film (~500 μm thick) were synthesized by arc discharge plasma jet CVD. The typical surface morphology is shown in Fig. 2(a). The diamond surface shows pyramidal shapes with mixture of triangular {111} and square {100} facets. The average dimension of the diamond grains are approximately 100 μm. The peak-to-valley surface roughness of the free-standing diamond films was about 20 μm.

Surface roughness was measured by a Dektak surface profilometer, which uses a mechanical stylus. The etching rate was obtained from the value of the etching depth divided by the number of laser pulses. The film surfaces were examined by scanning electron microscope.

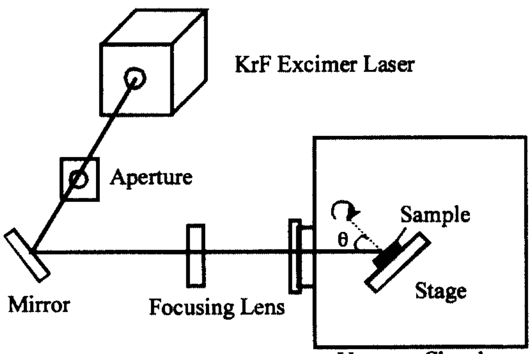

Fig. 1. Schematic diagram of laser processing for planarization of diamond films.

3. Results and Discussion

Fig. 2(b) shows the surface of a CVD diamond film after irradiation at normal incidence with a laser fluence of 2.0 J/cm^2 and with 500 pulses. The only center area of diamond films was modified with laser. The irradiated surface became much smoother compared to the original diamond surface (Fig. 2(a)), making ball shapes for each diamond grain. The tips and sharp edges of each diamond grain were especially much more modified.

Fig. 3 is shown for the explanation of the phenomena of smoothening of diamond films, especially of tips and edges of diamond grains after laser irradiation. The smoothening of diamond films is mainly caused by differences in etching rate between diamond tip areas and other surface areas. The peak regions have a higher fluence compared to the inclined surfaces

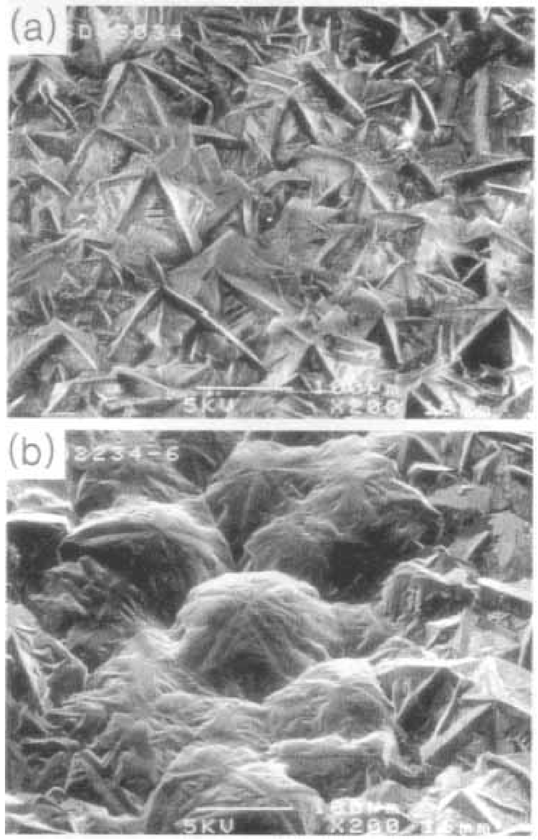

Fig. 2. Surface morphologies of diamond films. (a) original free-standing diamond, (b) normal irradiation (θ=0°) to the diamond surface (2.0 J/cm^2, 500 pulses).

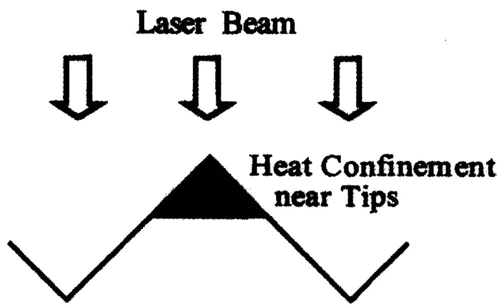

Fig. 3. Schematic illustration of laser-diamond interaction.

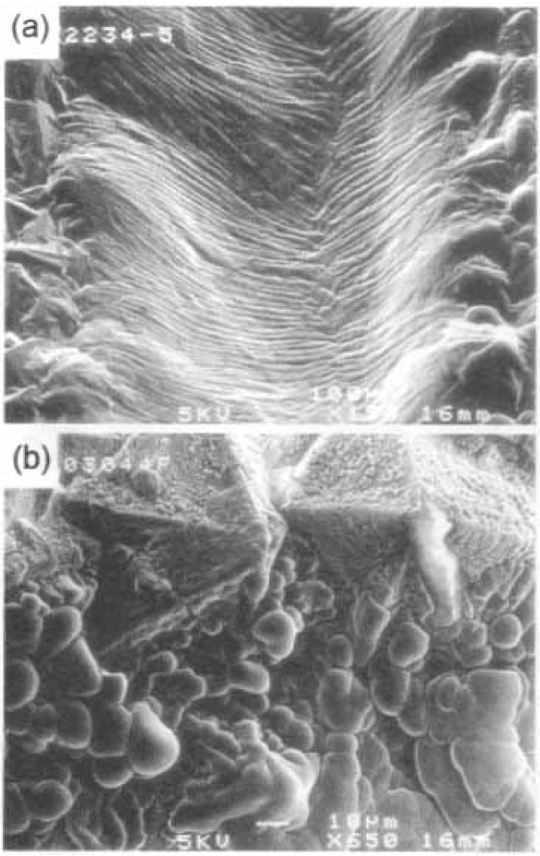

Fig. 4. Surface morphologies of diamond films. (a) normal irradiation ($\theta=0°$) to the diamond surface (3.5 J/cm^2, 2500 pulses), (b) boundary area of (a).

because of differences in projected surface area, leading to higher temperature in the peaks regions and then preferential etching. Heat dissipation effects are also a critical factor for smoothening of diamond surface. The surface asperities represent the areas where one-dimensional heat confinement takes place, whereas near the valley regions three-dimen-sional heat dissipation occurs. Thus, faster diamond etching rates are expected at the surface tips than the bulk, leading to planarization of the diamond film.

Fig. 4(a) shows the surface of a CVD diamond film irradiated at normal incidence with a laser fluence of 3.5 J/cm^2 and 2500 pulses. In this experiment, the sample surface was kept stationary during the irradiation process. The irradiated surface was deeply modified and more smoothed with many evenly spaced lines on the surface. This is called 'ripple', which is a kind of laser-induced periodic structure. The period of the surface ripple was approximately 10 μm, which is much wider than the wavelength of the laser. Irradiation with lower fluence of 1.5 J/cm^2 did not result in a periodic structure. Several mechanisms have been suggested for the generation of surface ripples including spatial beam homogeneities, interference effects between incident radiation and diffracted beams from surface imperfections, and shadowing effects from the surface asperities[10]. The ripple surface is more readily developed at higher beam intensities. It is still unclear that the spacing of ripples is approximately 10 μm even in experiments conducted at different laser wavelengths[7].

Fig. 4(b) shows the surface morphology of the surface adjacent to the laser-irradiated area. Spherical nodules composed of graphite or amorphous carbon are clearly observed. These nodules result from incomplete transformation of graphite into volatile gaseous species such as CO_x. When laser incidence was set at 45° to the diamond surface normal with laser fluences of 1 to 4 J/cm^2, roughness of the irradiated surfaces was not significantly improved.

Shown in Fig. 5 is the etching rate of the CVD diamond films plotted as a function of laser fluence for films irradiated at $\theta=45°$ using different gases (oxygen and ozone). Ozone was produced by an ozonizer. The oxygen feed gas flowed through a narrow gap between two concentric tube electrodes with a high DC voltage (6 kV) applied to these two electrodes to produce the ozone. The measured threshold energy for etching at 45° incidence was around 1.7 J/cm^2 irrespective of different gas atmospheres. The etching rate using ozone was lower than that using oxygen in this fluence range.

The surface morphologies of diamond films were

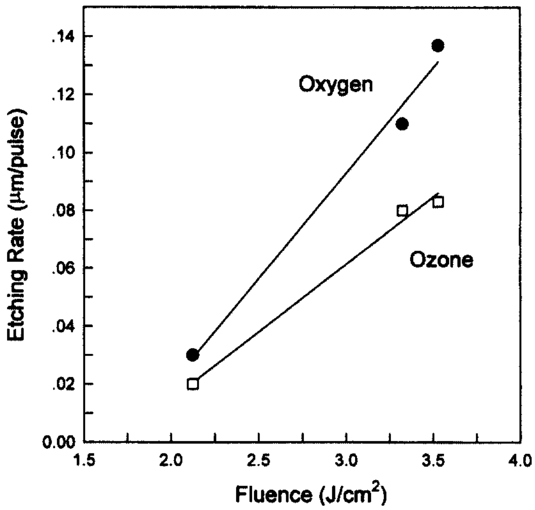

Fig. 5. Etching rate of diamond films as a function of laser fluence at $\theta=45^{\circ}$ under different gas atmospheres (oxygen, ozone).

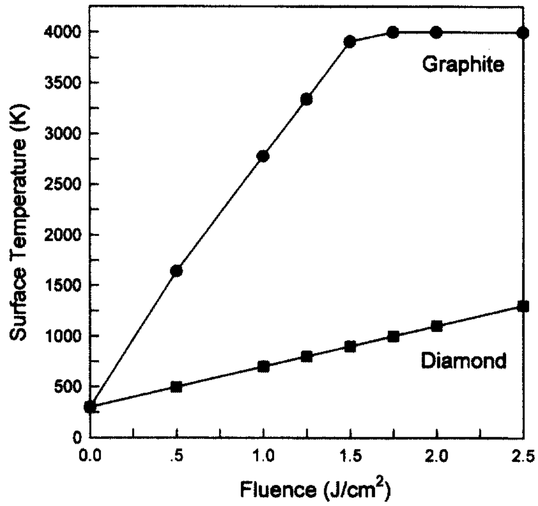

Fig. 6. The calculated surface temperature of diamond and graphite as a function of laser fluence.

observed after laser irradiation in different atmospheres as shown in Fig. 8. The surface of the diamond film processed in ozone, shown in Fig. 8(a), was found to be rougher with lower etching rate in comparison with the smooth diamond surface processed in oxygen (Fig. 8(b)). There may be several possible reasons for this;

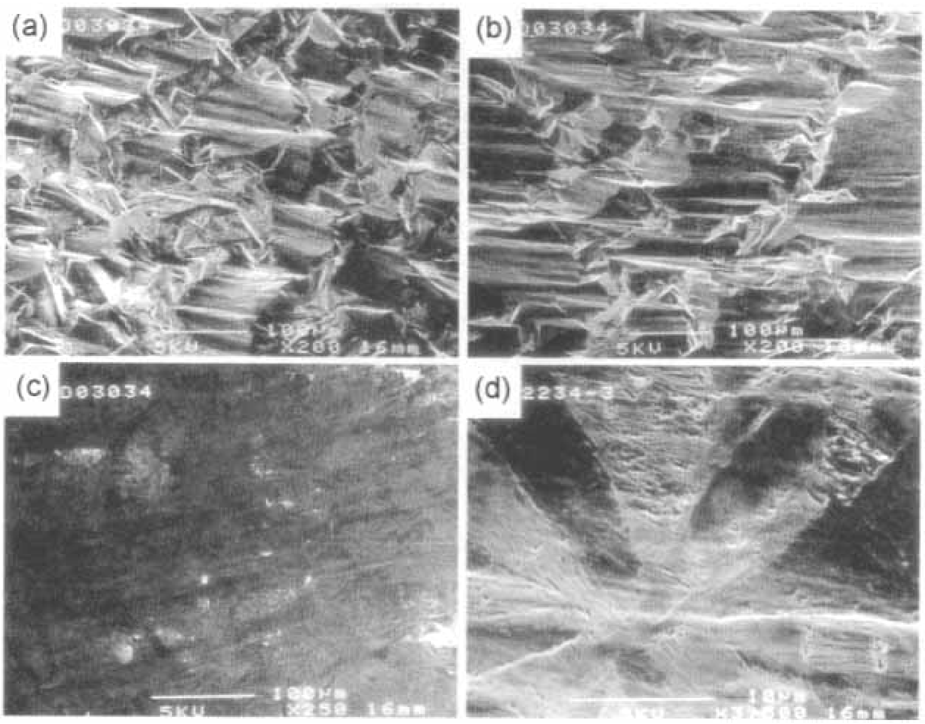

Fig. 7. Surface morphologies of diamond films as a function of number of pulses (a) 2400, (b) 4800, (c) 7200 with fluence of 2.1 J/cm^2 at $\theta=80^{\circ}$. (d) is the magnified image of (c).

Under oxygen atmosphere, the incident laser photon energy can be delivered to the film surface without much energy loss because the KrF laser energy (E=5.0 eV) is not enough for the dissociation of the O_2 bond (E=5.1 eV). Few amounts of atomic oxygen, if any, are near the film surface. On the other hand, under ozone atmosphere, some of the incident photon energy is absorbed by ozone due to its high absorption coefficient (α=290 cm^{-1})[12]. Namely, ozone gas blocks some amounts of the incoming laser light and lowers the laser energy density on the diamond surface, which results in an decrease of etching rate. Since more active atomic oxygen is produced on the diamond surface due to energy absorption and the corresponding decomposition of ozone to atomic oxygen, it plays an important role of selective chemical etching of the diamond surface microscopically depending on the crystal planes of each grain. Most diamond crystals have an octahedral shape formed by {111} planes in this sample. Compared to the relatively defect-free {100} planes, the {111} planes have many more defects and impurities which can absorb more laser energy, causing more heating and sublimation, and then resulting in faster etching rates. The etching rate of {111} planes when ozone is used will be more enhanced by more atomic oxygen compared to the one using oxygen. In other words, use of ozone will promote the preferential etching of certain planes, resulting in a rough surface.

Fig. 6 shows the calculated surface temperature of each element plotted as a function of laser fluence using SLIM (Simulation of Laser Interactions with Materials), a software package developed by John Viatella and Rajiv Singh[11]. The simulation assumed a single laser pulse and a planar surface. The sublimation temperature of graphite is around 4000 K and the graphitization temperature of diamond is around 900 K. Graphite absorbs much more photon energy than diamond due to larger absorption coefficient, leading to higher surface temperature with increasing fluence. The laser fluence satisfying both these surface temperatures which we call the threshold energy density, was 1.7 J/cm^2. This calculated value perfectly matched the experimental data at 45° laser incidence as seen in Fig. 5. Based on the data in Fig. 6, It is estimated that diamond is not directly etched away but transforms to graphite first and then sublimates, forming CO and CO_2.

Fig. 7 presents SEM images showing how the diamond surface changed as a function of number of laser pulses. A fluence of 2.1 J/cm^2 was applied at an angle of incidence of 80° to the surface normal. The original rough surface of the CVD diamond film (Fig. 2(a)) was progressively more etched away with increasing number of pulses, as shown in Fig. 7(a, b, and c). The peak-to-valley surface roughness was significantly reduced, going from 20 μm to 0.5 μm. From Fig. 7(d), which is a magnified image of Fig. 7(c), it can be clearly seen that preferential etching in accordance with crystal plane orientation was observed. Some crystal planes have a lot of fine streaks inside, which direction is pointing to specific direction, whereas other planes still have smooth surfaces without much streaks.

4. Conclusions

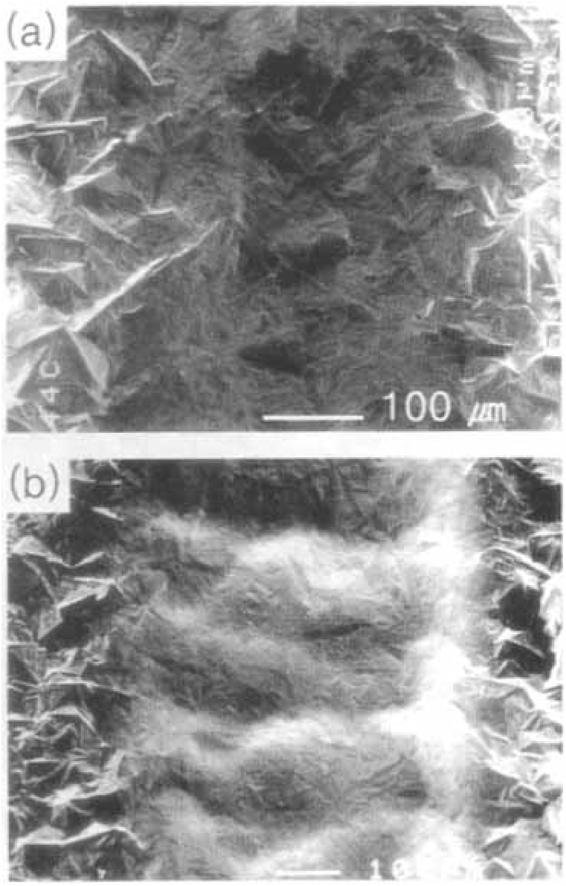

Fig. 8. SEM images of diamond surfaces at θ=45° under (a) ozone and (b) oxygen atmospheres with fluence of 2.2 J/cm^2.

The planarization of rough polycrystalline diamond films synthesized by DC arc discharge plasma jet CVD was attempted using KrF excimer laser pulses. The threshold energy density for etching of pure crystalline diamond was about 1.7 J/cm^2 from the experiment and fairly matched the simulation value. Preferential etching of a particular crystallographic plane was observed. The etching rate of diamond with ozone was lower than that with oxygen. When the angle of incidence was 80° to the film surface normal under oxygen atmosphere, the peak-to-valley roughness was significantly reduced, from 20 μm and 0.5 μm. The simulation helps for explanation of the planarization mechanism of diamond, which is firstly the transformation of a diamond to a graphite and then the sublimation of the graphite.

Acknowledgments

This paper was supported in 2000 by Research Fund, Kumoh National University of Technology.

References

1. W. Zhu, A. R. Badzian, and R. Messier, in Diamond Optics III, edited by A. Feldman and S. Holly, 1325 (Proc. Soc. Phot-Opt. Instrum. Eng. 1990) 187.
2. T. Zhao, D. F. Grogan, B. G. Bovard, and H. A. Macleod, in Diamond Optics III, edited by A. Feldman and S. Holly 1325 (Proc. Soc. Phot-Opt. Instrum. Eng., 1990) 142; Appl. Opt. 31 (1992) 1483.
3. A. Hirata, H. Tokura, and M. Yoshikawa, Thin Solid Films, 212 (1992) 43.
4. H. Tokura, C. -F. Yang, and M. Yoshikawa, Thin Solid Films, 212 (1992) 49.
5. S. Tezuka and M. Yoshikawa, J. Jpn. Soc. Precision Eng. 56 (1990) 2255.
6. A. Blatter, U. Bögli, L. L. Bouilov, N. I. Chapliev, V. I. Konov, S. M. Pemenov, A. A. Smolin, and I. V. Spitsyn, J. Electrochem. Soc. 91 (1991) 357.
7. U. B(gli, A. Blatter, S. M. Pimenov, A. A. Smolin, and V. I. Konov, Diamond & Relat. Mater. 1 (1992) 782.
8. M. Rothschild, C. Arnone, and D. J. Ehrlich, J. Vac. Sci. Technol. B, 4 (1) (1986) 310.
9. V. P. Ageev, L. L. Builov, V. I. Konov, A. V. Kuzmichev, S. M. Pemenov, Acedemician A. M. Prokhorov, V. G. Ral'chenko, B. V. Spitsyn, and B. I. Chapliev, Sov. Phys. Dokl. 33 (11) (1988) 840.
10. R. K. Singh and J. M. Fitz-Gerald, Nucl. Instr. And Meth. in Phys. Res. B, 121 (1997) 363.
11. R. K. Singh and J. Viatella, J. Met. 44 (1992) 22.
12. CRC Handbook of Marine Science, edited by F. G. Walton Smith (CRC press, Cleveland, Ohio, Vol I, 1974) 218.