The Korean Journal of Ceramics, 4 [1] 15 - 19 (1998)

Effect of Hydrogen Radicals for Ion Implanted CVD Diamond Using Remote Hydrogen Plasma Treatment (RHPT)

Jaihyung Won, Akimitsu Hatta, Hiromasa Yagi, Chunlei Wang, Nan Jiang,
Hyeongmin Jeon, Masahiro Deguchi*, Makoto Kitabatake*,
Toshimichi Ito, Takatomo Sasaki, and Akio Hiraki

Department of Electrical Engieering, Osaka University, Suita, Osaka 565, Japan,
**Central Research Laboratories, Matsushita Electric Industrial Co., ltd., Souraku-gun,*
Kyoto 619-02, Japan

(Received November 5, 1996)

Defects formation of Chemical Vapor Deposition (CVD) diamond on $^4He^{2+}$ irradiation and after remote hydrogen plasma treatment (RHPT) were investigated by cathodoluminescence (CL). As calculated in the TRIM simulation, the light elements of $^4He^{2-}$ can be penetrated into the diamond bulk structure at 3~4 μm depth. The effects of the implantation region were observed when 5 keV~20 keV electron energy (insight 0.3~4.0 μm) of CL measurement was irradiated to diamond at temperature 80 K. After the RHPT, rehybridization of irradiation damaged diamond was studied The intensity of 5RL center (intrinsic defect of C) was diminished The 2.16 eV center (N-V center) occurring usually by annealing could not be seen after RHPT. The diamond was rehybridized by hydrogen radicals without etching and thermal degradation by the RHPT.

Key Words : CVD Diamond, Ion Implantation, Cathodoluminescence (CL), Hydrogen Rehybridization, Remote Hydrogen Plasma Treatment (RHPT)

Chemical Vapor Deposition (CVD) of diamond films has made the production of diamond based semiconductor devices possible. Extremely low solubility and low diffusivity of impurities in diamond[1] make doping of diamond films with electrically active dopants difficult. Currently, p-type doping of CVD diamond is carried out using a mixture of a reaction gas and B_2H_6. The boron-doped films exhibit semiconducting behavior with resistivities as low as $10^{-2}\ \Omega cm^2$. Ion implantation is also widely used in silicon based device technology to obtain n-type doping. However, under certain implantation conditions irreversible amorphization of diamond can be induced. Also, it was shown that high energy electron or neutron irradiation induced neutral vacancy center and defects in the bulk diamond called GR1.[3] Further annealing results in a graphitization of the implanted samples[4] and the creation of new color centers[5] in synthetic diamond, therefore, it can not be used for damaged diamond recovering.

Hydrogen atom may induce rehybridization of the damaged area and sp^3 bonding can be obtained once again after hydrogen plasma treatment[6] J. C. Angus[7] suggested that the atomic hydrogen could stabilize the diamond surface by satisfying the dangling bond. The amorphous layer on the diamond film surface, produced by hot filament for diamond surface stabilization [8] However, the effect of hydrogen plasma is not fully understood yet.

In this paper, because of the effect of profound implantation, the diamond films the implanted with the light $^4He^{2+}$ elements ion in CVD are studied by low temperature cathodoluminescence (CL). Also. the effect of remote hydrogen plasma treatment (RHPT) on the CL spectra of CVD diamond film is reported. It is currently supposed that hyrogen may induce rehybridization and stabilization of the diamond layer after hydrogen plasma treatment.[6,7]

Experimental Procedure

Diamond films were grown on single crystal of p^+ Si substrates by microwave plasma CVD. An ultrasonic pretreatment with diamond powders was carried out for all of the substrates. The gas mixture used in the experimental growth consisted of 100 sccm of 10% CO diluted in H_2. The following growth conditions were used: total pressure 45 Torr; microwave power 250 W, time 8 hr and substrate temperature 900°C. The single-crystal CVD diamond was deposited around 3 μm depth region of diamond. Ion density was ~10^{15} ions/cm^2. There were calculated by the Transport of Ions in Matter (TRIM) simulation.

Microwave H_2 plasma treatments were performed in the same MW reactor used for the film deposition. A 90

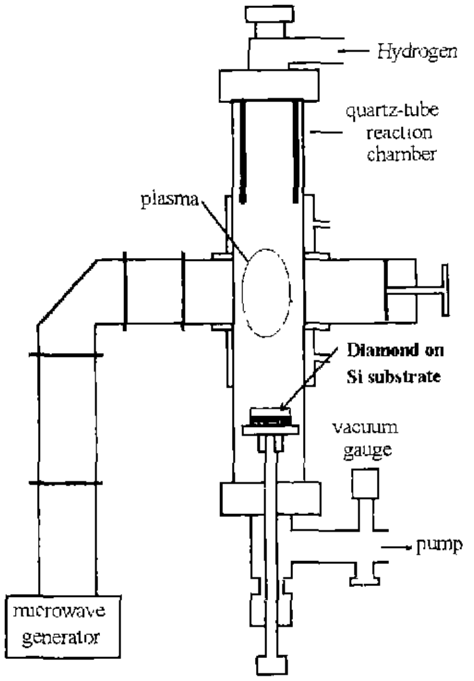

Fig. 1. Remote Hydrogen Plasma Treatment (RHPT) were performed by MW reactor. That was treated far apart around 10 cm from the discharge area.

sccm pure H_2 plasma was used for 10 min at a substrate temperature of about 900°C. On the contrary, vacuum annealing treatment was perfor med at ~10^{-6} Torr, 900°C for 10 min. In thr RHPT, it is same condition to conventional hydrogen plasma treatment except for distance from the pasma ball. That was treated far apart around 10 cm from the discharge area for 0.5 hr to 2 hr, as seen in Fig. 1. It is likely that temperature of substrate was above 50°C and below 500°C. Scanning electron microscope (SEM) was used for CL measurements. Irradiation condition were; 5 kV~20 kV acceleration voltage and 0.05 μA/cm^2 current density. In order to measure CL spectra. SEM was equipped with a parabolic mirror in front of the specimen, a monochromator and a photomultiplier tube (PMT). The specimen was cooled down to liquid nitrogen temperature during CL measurement. In the case of CL measurement the electron beam acceleration voltage 5 kV~20 kV, produced a electron penetration depth about the 0.34 μm~4.26 μm as calculated by equation $L = 0.018\ V^{1.825}$, which study of the diamond allowed the layer properties.[9]

Results and Discussion

The typical CL spectra of undoped CVD diamond is shown in Fig. 2 (a). It was ovserved that CL spectrum contains a peak centered at wavelength 425 mm (2.9 eV), called band-A. Also, free cexiton recombination radiation peak was detected which indicates good crystallinity.[10] Fig. 2 (b) shows a CL spectrum of undoped CVD diamond after He ion implantation. It is shown that the 4 μm electron penetration area is achieved by CL the same as found out implantation region. The CL spectrum of undoped specimen has two relatively broad peaks after He ion irradiation in Fig. 2 (b). One of them is the same band-A peak with 3.19 eV (389 nm) center, the 3.19 eV center is caused by an interstitial carbon produced by the radiation damage together with a single nitrogen atoms.[11] The other is called 5RL center, suggesting the presence of intrinsic defect in the undoped diamond.[12-15] Collins *et al.* showed that the local-mode peaks in the 5RL are associated with vibration of a carbon atom and proposed that this is the interstitial produced by radiation damage.[14] The 5RL center contains four narrow peaks located at every 0.234 eV. It was found that the 5RL center appears in the CL spectra when intrinsic defects were induced by ion implantation or high energy electron irradiation.

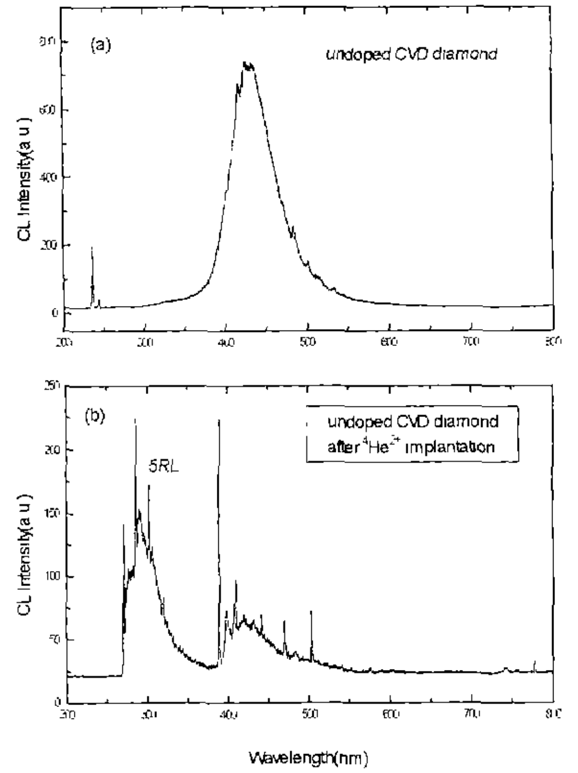

Fig. 2. CL spectra of CVD diamond (a) the typical undoped CVD diamond and (b) $^4He^{2+}$ ion irradiated CVD diramond.

If the intrinsic defect of diamond can be rehybridized by hydrogen radicals, the hydrogen plasma treatment can be used for diamond reconstruction. After ordinary hydrogen plasma treatment, the luminescence spectrum of 2.16 eV center (575 nm) appeared whose CL spectra is shown in Fig. 3 (a). The 2.16 eV center originates from a vacancy coupled with nearest interstitial nitrogen atoms.[16-18] It was proved that vacuum-annealing (900°C) process induced migration of vacancies, resulting in the N-V center as shown in Fig. 3 (b). Additionally, R. Kalish[19] reported the vacancies formed during the collision

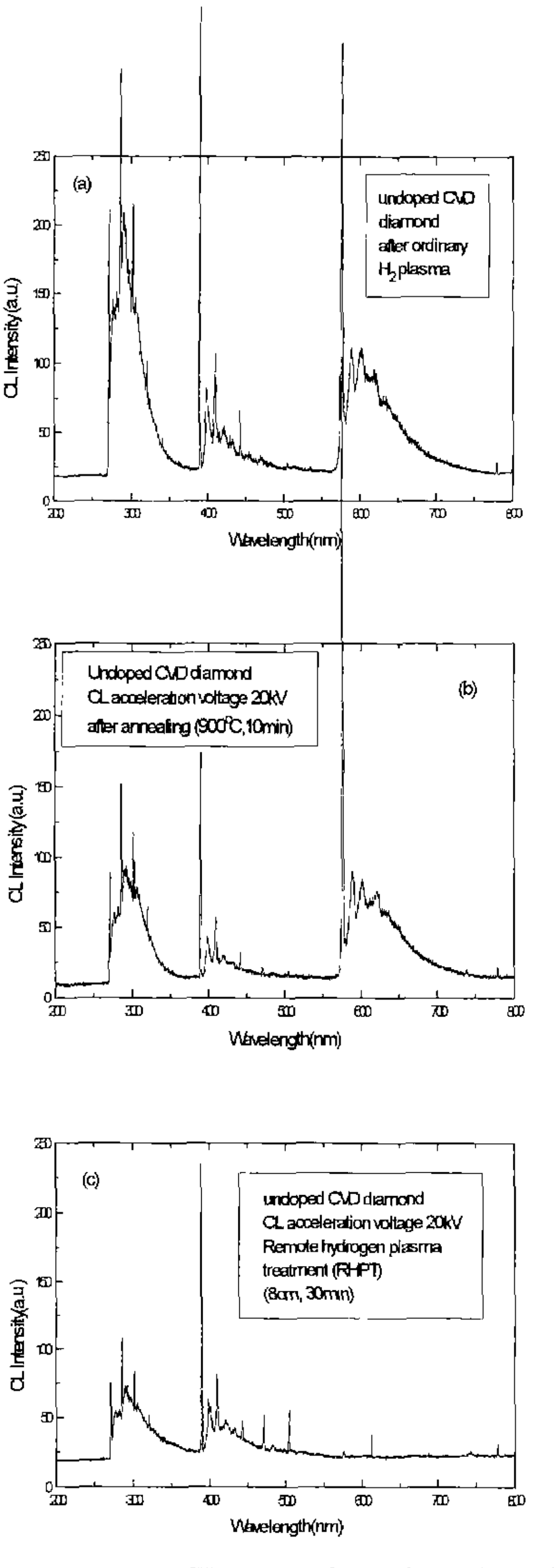

Fig. 3. Cl spectra of CVD diamond (a) after ordinary hydrogen plasma treatment, (b) after 900°C vacuum annealing. The luminescence spectrum of 2.16 eV center (575 nm) appeared. Fig. 3 (c) CL spectra of after Remote Hydrogen Plasma Treatment (RHPT). This is shown N-V center was not observed by CL investigation for 30 min RHPT. The intrinsic defect related peak (5RL) diminshed as proved by CL spectra

cascade can be mobile over 500°C. These facts suggest that this center is not related to the implanted element, but to the implantation and plasma-annealing temperature (900°C) induced a defect (N-V center). Thus, the ordinary hydrogen plasma treatment of this film results in temperature degradation of diamond bulk site before rehybridization is achieved.

Furthermore, comparison of the cross section SEM images before and after ordinary hydrogen plasma treatment indicates relatively high (0.7 μm/h) etching rates of the undoped films [20] Hence, the hydrogen plasma treatment of this film results in the etching of surface layer before reconstruction is carried out.

Unlike ordinary plasma treatment the RHPT did not induce the etching effect which was found out by SEM morphology and AFM investigation. Also, the RHPT did not lead to high temperature degradation of diamond. This is shown in Fig. 3 (c) the N-V center was not observed by CL investigation. In the same time after RHPT, the intrinsic defect related peak (5RL) diminished as proved by CL spectra. It is shown that 30 min RHPT induces the reconstructing stage of the intrinsic defect of the C-C diamond bond. Thus, experimental data show that RHPT results in the rehybridization of bulk-site defects inducing sp^3 hybridized carbon atoms without etching and high temperature degrdation.

In homoepitaxial CVD diamond, Fig. 4 (a) shows a CL spectrum of CVD single diamond after He ion implantation. The CL spectrum of specimen has two relatively broad peaks the same as poly-crystalline CVD diamond, called band-A and 5RL. The electron beam acceleration voltage of the CL measurement was 15 kV, which caused penetration depths about 2.5 μm.[9] It is shown that the 2.5 μm electron penetrated region is achieved by CL the same as found out implanted region. After RHPT, the shallow areas (0.3 μm) of CVD single crystal layer were characterized by CL as shown in Fig. 4 (b). The intrinsic defect related peaks (5RL) diminished after 1 hr RHPT, as seen from CL spectra. The reconstruction and stabilization of defect structure progressed after 1 hr that could be explained by longer duration of the RHPT.

In this case, using the electron-penetration CL measuring technique a deep-level layer (2.5 μm) rehybridization of the single-crystal CVD diamond was found as can be seen in Fig. 4 (c). After 2 hr RHPT the intrinsic defect related peaks (5RL) diminished as measured by deep region CL spectra which is caused a electron penetration 2.5 μm of the single crystal CVD diamond.[9] It seems that the hydrogen radicals diffused from the surface layer into the bulk structure. It was taken by RHPT for 1 hr from the surface to 0.3 μm lyer then, for 2 hrs from the surface to 2.5 μm region of CVD single diamond. It seens that hydrogen radicals can diffuse during RHPT causing defect areas such as dislocation or misorienta-

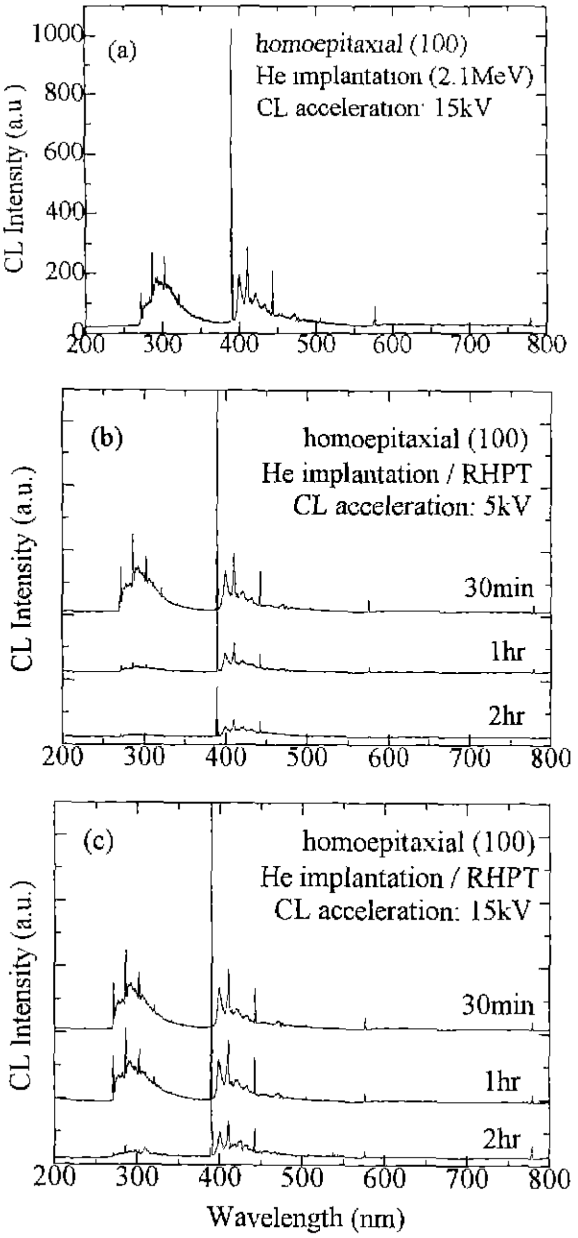

Fig. 4. (a) shows a CL spectra of CVD single diamond after He ion implantation. (b) The CL spectra of after time duration RHPT. The depth of single-crystal layer was measured in order to study such thickness (0.3 μm) by CL penetration measuring technique (5 kV). The 5RL diminished after 1 hr RHPT. (c) The depth of single-crystal layer was measured the such thickness (2.5 μm) by CL (15 kV). The 5 RL diminished after 2 hr RHPT.

tion of the diamond. Consequently it seems necessary to induce rehybridization in order to reconvert the damaged diamond. In agreement with etching effect were proposed by direct induced ordinary hydrogen plasma treatment that etch pits of (100) single crystal diamond are developed proibably on lattice defects such as dislocations by hydrogen.[21] N. Lee, *et al.*[22] propesed that etch pits in homoepitaxial diamond are caused by the degree of surface misorientation of substrates. Therefore, we understood that hydrogen radical was infused into the diamond structure such as defects by RHPT. The interstitial carbon atoms could be mobilized to sufficent recovering during RHPT by diffusion of hydrogen radical effect.

According to an additional report provided by J. E. Prince[23] substantial diffusion of self-interstitials occurs at about 50°C. Sine, the exact temperature of the diamond substrate could not be measured in this experiment, it is likely that the temperature of substrate was above 50°C (diffusion of self-interstitial)[23] and below 500°C (immobile vacancy).[19]

These facts, together with CL observations leads to a conclusion that RHPT is a useful technique for recovering implantation damaged diamond without etching and affection by a tempeerature annealing.

Summary

The CL of the implantation region before and after RHPT was ovserved when 5 keV~20 keV electron energy was irradiated to diamond using CL penetration-observing technique at 80 K.

After the RHPT, the N-V center could not be seen which occurred by annealing. The intensity of 5RL center (intrinsic defect of C) was diminished as measured by deep region CL spectra. It was shown that the hydrogen radicals diffused from the surface layer into the bulk structure. Consequently it seems necessary to induce rehybridization in order to recover the damaged diamond. It was shown that the RHPT is a useful technique for recovering implantation damaged diamond.

The authors wish to thank S. Sonoda, K. Ogawa, and Nishimura for their assistance. This work was partly supported by a the Research Project of Industry and Academy Sponsored by Japan Socety for the Promotion of Science.

References

1. J E Field, ed., The properties of Diamond, (Academic Presss, London, 1979).
2. A. T. Collins, Mater Res. Soc Symp. Proc., 162, 3 (1990).
3. P. J. Dean, Phys. Rev. A. 139, 588 (1965).
4. R. Karish, T. Bernstein, B. Shapiro and A Talmi, Radiat. Effects, 52, 153 (1980).
5. J. Walker, Rep. Prog. Phys. 42, 1605 (1979).
6. B. B. Pate, Surf. Sci. 165, 83 (1986).
7. J. C. Angus and C. C Hayman, Science, 241, 913 (1988).
8. W. Engel, D. C. Ingram, J. C. Keay and M. E. Kordsch, Diamond Relat. Mater , 3, 1227 (1994).
9. G. Davies, The properties of Diamond. ed., J. E. Field, Chap. 5 III. Production of CL (Academic press, London, 1979).
10. H. Kawarada, Y. Yokota, T. Sogi, H. Matsuyama and A Hiraki, SPIE Diamond Optics III 1325, (1990)
11. A. T. Collins and G. S. Woods, J. Phys. C: Solid State

Physics. 20, 797 (1987).
12. J. Mazzaschi, J C. Brabant, M. Brousseau and F. Viollot, Rev. Phys. Allp. 15, 9 (1980).
13. A. T. Collins and P. M. Spear, J. Phys. C. 19, 6845 (1986).
14. A. T. Collins, G. Davies, H. Kands and G. S. Woods, J. Phys. C. 1363 (1988).
15. J. Ruan and W. J. Choyke, J. Appl. Phys. 69, 9 (1988).
16. A. T. Collins, M, Stanley and G. S. Woods, J. Phys. D. 20, 969 (1987).
17. A. M. Zaitsev, A. A. Gippius and V. S. Vavilov, Soviet Phys. -Semicond. 16, 252 (1982)
18. L. H. Robins, L. P. Cook, E. N. Farabaugh and A. Feldman, Phys. Rev. B. 39, 367 (1989).
19. R. Kalish, Kiamond and Related Materials, 2, 621 (1993).
20. J. H. Won, A. Hatta, H. Yagyu, N. Jiang, T. Ito, T. Sasaki, A. Hiraki, Appl. Phys. Lett. 68, 20 (1996).
21. M. Mitsuhashi, S. Kawarada, S. Ohya and F. Togashi, Appl. Surf. Sci. 60/61, 565 (1992).
22. Naesung Lee and andrzej Badzian, Appl. Phys. Lett. 66, 17 (1995).
23. J. E. Prince, Radiat. Effects Lett., 76,79 (1983).