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Formation of conductive layers on singlecrystalline diamond by Excimer laser irradiations

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Abstract: *For formation of conductive layers on singlecrystalline diamond, excimer-laser-induced surface doping technique was employed to singlecrystalline diamond substrates. Nano-second pulsed laser with a wavelength of 193 nm was applied and irradiated upon immersed substrate in boric acid which acts as a dopant source. Surface conductivity progressively enhanced with increasing laser fluence and number of laser shots. Furthermore, resistivity decreased with increasing temperature, which implies that the surface layers generated by laser irradiations are semiconducting. Depth profile from secondary ion mass spectroscopy showed successful incorporation of dopant species up to 40 nm depths below the surface. Results are promising as a new method for surface doping of single crystalline diamond.*

Keywords: ArF excimer Laser; singlecrystalline diamond; Boron doping.

1. INTRODUCTION

Diamond is a promising wide bandgap semiconductor with outstanding electrical and optical properties, applicable to devices that handle more power with higher efficiencies than those of conventional semiconductors [1-3]. Owing to its favorable inherently physical and electrical properties such as a high breakdown voltage combined with high mobility, negative electron affinity, small dielectric constant, and prime radiation hardness. Thus, diamond is an ideal candidate for electronic and optical applications such as ultraviolet light emitting diodes (UV-LED), cold cathode electron emitters, and high-power and high-frequency devices [1].

The fabrication of diamond devices has serious problems in doping. It is extremely difficult to form ohmic contacts on doped diamond as well. In addition, it requires relatively high temperature treatments, which is harmful for devices that cannot undergo high temperatures. for diamond, the doping must be achieved during the crystalline growth by chemical vapor deposition (CVD) [4], which is completely different from other existing semiconductors that can be treated thermally after deposition.

Recently laser-induced doping in acid liquids have received attention as a new doping method [5]. Since it can provide a low thermal-damage owing to its local and very short heating mechanism. In this work, we applied laser-induced doping method to singlecrystalline diamond, for the first time to our knowledge. Doping of boron into singlecrystalline diamond is discussed from the chemical compositionally and electrically viewpoints.

2. EXPERIMENTAL PROCEDURES

Singlecrystalline diamond (100) plates (Ib) (Sumitomo Electric Industries, high-pressure and high-temperature conditions of 5 GPa and 1,300 ºC or higher (HPHT)) were immersed in the boric acid solution (H_3BO_3 (2%). and ArF excimer laser (Gigaphoton Inc. wavelength: 193 nm) beams were irradiated on the immersed diamond substrates as schematically shown in Figure 1. Dopant liquid was only few millimeters above the sample surface to ensure full coverage of irradiated area. The shape of the laser beam was rectangular with a size of 200 μm × 400 μm. The laser beam irradiation was carried out at different frequencies and different laser fluences.

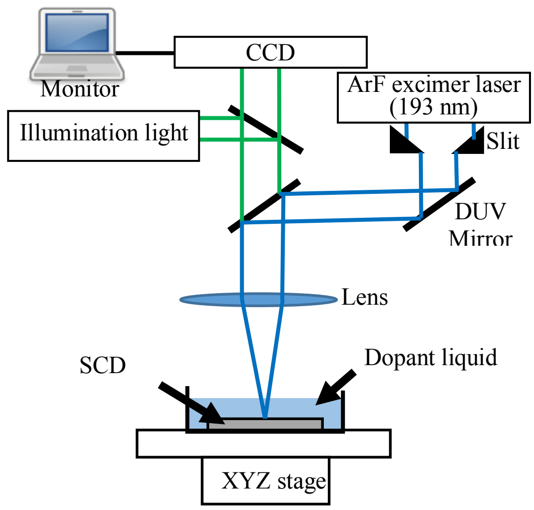

Figure 1. Schematic diagram of experimental setup for laser-induced doping.

Current-voltage characteristics of irradiated areas were performed on the range of (-10 to 10 V at different number of shots and temperatures using a two probe source meter (Keithley 2400) after the cleaning of the surface twice with a boiling acid (H_2SO_4:HNO_3[3:1]) at 220° C for 50 min to ensure graphitic layer removal from the surface. Probe heads were directly contacted with the sample surface. The incorporation of boron atoms into diamond was investigated by Secondary Ion Mass Spectroscopy (SIMS).

3. RESULTS AND DISCUSSION

Figure 2 illustrates image of singlecrystalline diamond after irradiation with different frequency and number of shots. Obviously, the laser-irradiated areas have different colors as compared with non-irradiated areas, and the color gradually become dark with increasing number of shots. Black debris on the irradiated areas, which might be graphitic, were peeled off from the surface by the boiling acid treatment. Results shows that singlecrystalline diamond hardly damaged even at a maximum fluence of 5 J/cm^2.

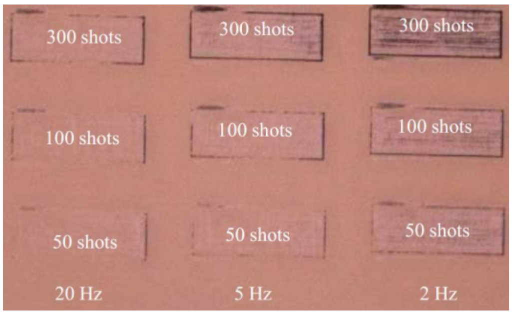

Figure 2. Optical images of areas laser-irradiated at 5 J/cm^2 and different irradiation conditions.

I-V curve measurements indicated that the electrical conductivity increases with increasing fluence and number of laser shots. Activation energy was estimated from the temperature dependence of the electrical resistance. The activation energy decreases with increasing shot number, which might be attributed to an increase in the B/C ratio as shown in Figure 3.

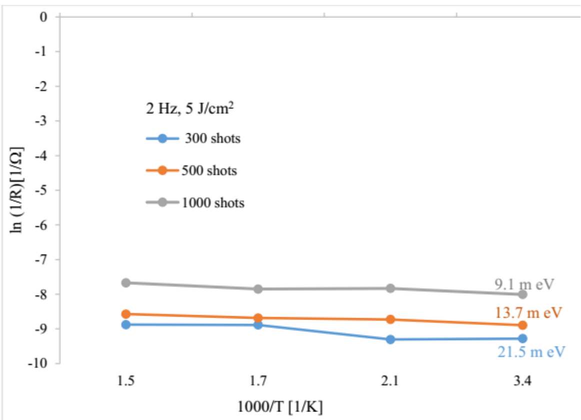

Figure 3. Arrhenius plot of electrical conductivity for laser-irradiated substrate at different shot numbers.

This evidently indicates that laser-irradiated surface is semiconducting. Which means that the laser-induced doping might be beneficial for facilitating formation of ohmic contacts between diamond and electrodes.

Boron incorporation depth profile was investigated by SIMS. The measurements were carried out near the center of the irradiated area. Curves evidently reveals the incorporation of boron to singlecrystalline-diamond by laser irradiation in a depth range from 0 to 40 nm. It is important to consider that the sample used for SIMS measurements was irradiated at a lower laser focusing compared with all other samples used for electrical measurements. The sample prepared at higher laser focusing has conductivity that is one order of magnitude higher than that prepared at lower focusing (used for SIMS) under same irradiation conditions. With focus enhancement, a higher concentration and slightly deeper incorporation is expected. This demonstrates that laser-induced doping is applicable to boron doping of singlecrystalline diamond.

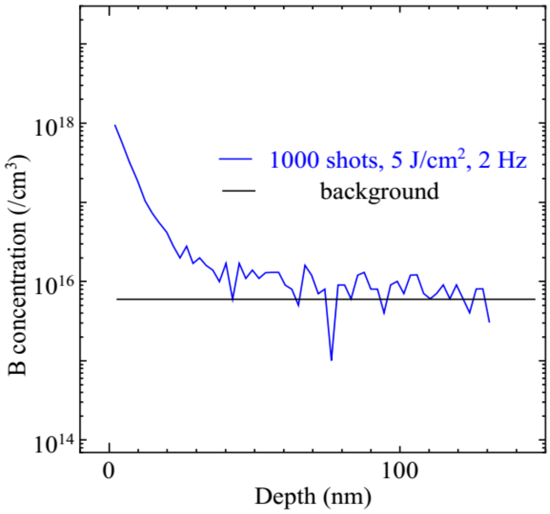

Figure 4. SIMS depth profile of Boron doped Singlecrystalline diamond.

The process here is different from thermal doping method; it is most likely photochemical doping. the process starts with the absorption of the laser pulse by the substrate, due to fast electron-phonon energy transfer, we assume that the photons energy is locally and instantaneously converted into heat then a plasma plume expands into the surrounding liquid, accompanied by the emission of a shockwave through the substrate itself. During this time and before ultra-fast quenching, the surface remains ablated for a short time which was proved to be same as laser pulse duration (20 ns) during which reaction with dopant source and incorporation occurs.

4. CONCLUSION

Laser-induce doping in liquids containing dopant elements is applied to singlecrystalline diamond. It certainly increased the electrical conductivity of the surface. Although the evidence of substitutional doping is not obtained, it should be applicable to facilitating the formation of ohmic contacts between n-type/p-type diamond and metallic electrodes. This method has a potential for exploring new dopant elements that have not experimentally investigated due to difficulties in the doping during the deposition so far.

5. ACKNOWLEDGEMENT

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