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Abubakr, Eslam

Department of Applied Science for Electronics and Materials, Kyushu University | Department of
Electrical Engineering, Faculty of Engineering, Aswan University

Zkria, Abdelrahman

Department of Applied Science for Electronics and Materials, Kyushu University | Department of
Physics, Faculty of Science, Aswan University

Ohmagari, Shinya

Advanced Power Electronics Research Center, National Institute of Advanced Industrial Science
and Technology

Imokawa, Kaname

Graduate School of Information Science and Electrical Engineering, Kyushu University

他

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Characterization of phosphorus doped singlecrystalline diamond prepared by Excimer-Laser Irradiations

Eslam Abubakr^{1,2*}, Abdelrahman Zkria^{1,3}, Shinya Ohmagari⁴, Kaname Imokawa⁵, Yūki Katamune⁶, Hiroshi Ikenoue⁵, and Tsuyoshi Yoshitake^{1*}

¹Department of Applied Science for Electronics and Materials, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

²Department of Electrical Engineering, Faculty of Engineering, Aswan University, Aswan 81542, Egypt

³Department of Physics, Faculty of Science, Aswan University, Aswan 81528, Egypt

⁴Advanced Power Electronics Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan

⁵Graduate School of Information Science and Electrical Engineering, Kyushu University, Fukuoka 819-0395, Japan

⁶Frontier Research Academy for Young Researchers, Kyushu Institute of Technology, Kitakyushu, Fukuoka 804-8550, Japan

E-mail: abubakr_eslam@kyudai.jp ; tsuyoshi_yoshitake@kyudai.jp

Abstract: In this work, Laser-induced surface doping technique was applied to singlecrystalline diamond substrate. ArF excimer laser with a wavelength of 193 nm and pulse duration of 20 ns was employed and irradiated upon immersed substrate in Phosphoric acid that acts as a dopant source. Surface resistivity gradually decreased with increasing laser fluence and number of pulsed laser irradiation. Furthermore, Conductivity enhanced with increasing temperature, which implies that the surface layer generated by irradiation is semiconducting. Depth profile was measured by secondary ion mass spectrometry. results confirmed the incorporation of phosphorus atoms up to 30 nm depths from the surface. Results are promising as a new method for doping of single crystalline diamond. However, the mechanism of the phosphorus incorporation requires more considerations.

Keywords: ArF excimer Laser; singlecrystalline diamond, Phosphorus Doping.

1. INTRODUCTION

Diamond is a promising wide bandgap semiconductor with outstanding electrical and optical properties combined with extremely large thermal conductivities, applicable to devices that handle more power with higher efficiencies than those of conventional semiconductors [1-3]. In addition, 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].

Doping for fabrication of diamond devices represent a serious problem, physically and technically. Whereas Boron is a representative dopant for the production of p-type conduction, finding a suitable dopant for producing n-type conduction at room temperature is still challenge. Although, phosphorus and nitrogen are commonly used for production of n-type conduction, in diamond they form deep donor levels. It is extremely difficult to form ohmic contacts on phosphorus-doped diamond. In addition, for diamond, the doping must be achieved during the crystalline growth by chemical vapor deposition (CVD) [4-5], which is completely different from other existing semiconductors that can be treated thermally after deposition.

Recently laser-induced doping in acid liquids have been applied to SiC and its effectivity is experimentally proved [6]. In this work, we applied laser-induced doping method to singlecrystalline diamond, for the first time to our knowledge. Doping of phosphorus into singlecrystalline diamond is discussed from the chemical compositionally and electrically viewpoints.

2. EXPERIMENTAL PROCEDURES

Singlecrystalline diamond (100) plates (Ib) (Sumitomo Electric Industries) were immersed in a phosphoric acid solution (85%). 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 $150\ \mu\text{m} \times 350\ \mu\text{m}$. The laser beam irradiation was carried out at different frequencies and different laser fluence.

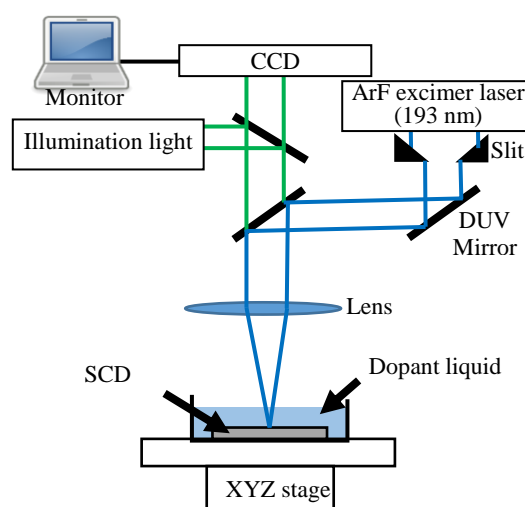


Figure 1. Schematic diagram of experimental setup for laser-induced doping.

The surface electrical resistance was estimated from current-voltage (I-V) measurements by a two probe method using a source meter (Keithley 2400) after the cleaning of the surface twice with a boiling acid ($\text{H}_2\text{SO}_4\text{:HNO}_3[3:1]$) at 220°C for 30 min to ensure graphitic layer removal from the surface. Probe heads were directly contacted with the sample surface. The incorporation of phosphorus 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 fluences and number of shots. Combined with SEM Image, results show that singlecrystalline diamond hardly damaged even at a maximum fluence of 3.9 J/cm^2 .

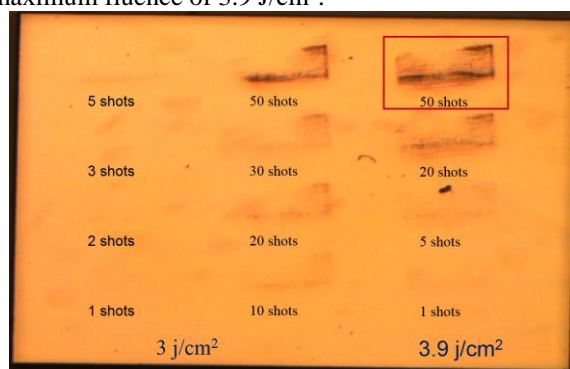


Figure 2. Optical microscopic image for Singlecrystalline diamond substrate after irradiation

I-V curve measurements indicated that the electrical conductivity increases with increasing fluence and number of laser shots as shown in Figure 3.

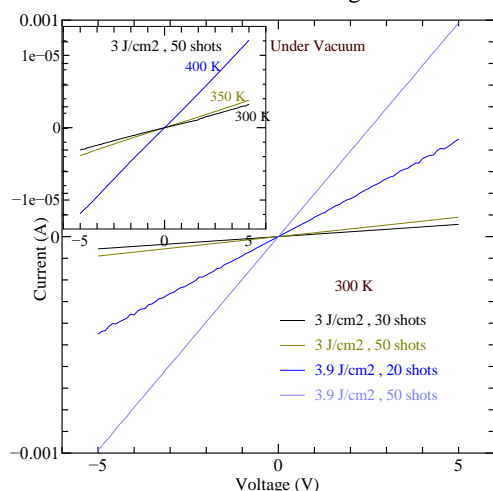


Figure 3. surface resistivity variation with Laser fluency, shots and temperature

Electrical conductivity is also enhanced with increasing temperature from 300 to 400 K, as shown in the inset of Figure 3, which evidently indicates that laser-irradiated surface is semiconducting. This means that laser-induced doping might be beneficial for facilitating formation of ohmic contacts between diamond and electrodes.

Phosphorus depth profile was investigated by SIMS. As shown in Figure 44, the incorporation of phosphorus at depths of up to 30 nm is achieved by increasing number of shots and reducing interval time between successive shots. This demonstrates that laser-induced doping is applicable to phosphorus doping of singlecrystalline

diamond. we consider that a reason for the non-incorporation of the 30 shots sample is that the interval time between laser shots might be longer than the relaxation time of thermal diffusions in diamond, which degrade heat accumulation and temperature increase for inducing the phosphorus incorporation phenomena.

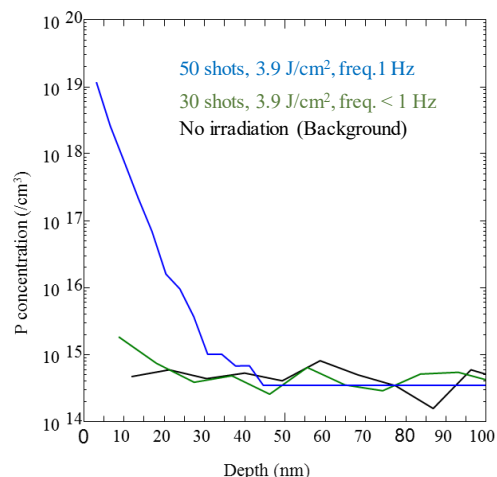


Figure 4. SIMS depth profile of phosphorus doped Singlecrystalline diamond.

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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