Ion Shower Doping Effect in Diamond and Diamond-Like Carbon Films

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ABSTRACT

We have studied the possibility of n-type doping in diamond and DLC films. After ion doping of either p-type or n-type, the electrical conductivities were remarkably increased and conductivity activation energies were decreased. The Raman intensity at 1330 cm^{-1} decreases slightly by ion doping of 7.2×10^{16} cm^{-2}. The increase in conductivity by ion doping appears to be arised from the combined effects by substitutional doping and graphitization by ion damage.

1. INTRODUCTION

Diamond-Like Carbon (DLC) films are of interest because of their outstanding properties, such as high mechanical hardness silmilar to diamond, optical transparency at IR region, high electrical resistivity, and chemical inertness. The DLC films have been prepared by various methods, for example by ion deposition, bias sputtering, and plasma decomposition of hydrocarbon gases [1]. The ion bombardment on the growing surface by positive ions seems to be an important parameter to grow DLC films[2,3].

DLC films can be applied as an electron emission material or over-layer coating on cathode for Field Emission Display (FED). In FED, electrons emitted under electric field are bombarded on phosphor screen. The AD (amorphic diamond) films[4,5] emiting electrons at electric field lower than 20 V/micron could be used to fabricate diode-like FED because of its low work function.

Standard doping techniques such as diffusion or introduction of impurities during crystal growth are hardly applicable to diamond, so that the most promising way to diamond in a controlled way is by means of ion implantation. The succesful use of this technique, however, requires finding annealing conditions which will drive the implants into electrically active and restore the diamond crystal structure, a task which is particularly complicated by the tendancy of damaged diamond to turn into graphite. The p-type diamond film could be grown by using a diborane mixture in a plasma region. However, the n-type doping in diamond and DLC films is considered to be nearly impossible. In low p-type (5.4×10^{15} cm^{-2}) implantations, no noticeable graphite layer could be found. On the other hand, when implanted dose is exceed 5.4×10^{15} cm^{-2} conductivity is higher than 10^2 S/cm and activation energy decreases to 0.024 eV[6]. At implantation dose of 2×10^{15} cm^{-2}, the sheet resistance decreases to a value of less than 10^7 $\Omega/\square$ by 10^{16} cm^{-2} ion dose. It can be seen that the saturation resistance decreases as the implantation temperature increases from room temperature to 553 K[7].

2. ION SHOWER DOPING APPARATUS

The ion shower doping system consists of the plasma generating and acceleration regions[8]. A gas mixture of 1 % PH_3 diluted in He or 1 % B_2H_6 diluted in H_2 was introduced into plasma chamber. The introduced gas was discharged by RF (13.56 MHz) power at a pressure of $\sim10^{-4}$ torr. The diameter of

ion beam was about 20 cm and ion current was fixed at 5 mA throughout this work. To avoid the flow of secondary electrons into the high voltage grid, a grounded grid was set between the high voltage (up to DC 30 kV) grid and the sample stage. The double grids are effective in suppressing charge accumulation during ion doping. Ions diffused from the plasma region to the aperture of biased mesh are accelerated by a potential difference between two meshes and are radiated onto samples. Doping temperature was varied from room temperature to 250 °C.

3. RESULTS

3.1 Doping effect in diamond films

Diamond films were deposited by HFCVD (Hot-Filament Chemical Vapor Deposition), one of popular methods for growing diamond films[9]. The reactant gas(H_2 and CH_4) was excited by a heated tungsten. Substrate and filament temperatures were fixed at ~700 °C and ~2200 °C, respectively.

Figure 1 shows Raman spectra of the diamond films grown by HFCVD. A sharp diamond TO modes at 1335 cm^{-1}, and broadbands at ~1350 cm^{-1}, ~1580 cm^{-1} caused by trigonal coordinated (sp^2) bonds appear in the spectrum. The Raman peak appears at 1335 cm^{-1} for the undoped diamond film as Fig. 1(a). This position is shifted by 2 cm^{-1} from the natural diamonds which occurs at 1332 cm^{-1}. This suggests that a residual compressive stress was present in the film due to the differences in thermal expansion coefficients between substrate Si and diamond film. When the films were doped with PH_3 ion, the peak position was shifted to higher wavenumber (1337 cm^{-1} at 7.2×10^{16} cm^{-2} ion dose) compared with undoped diamond films, implying that PH_3 plasma doping increases the residual compressive stress or changes the grain size which can also affect the peak position. Another interesting feature of the Raman peak was the intensity of the sp^2 peak at 1580 cm^{-1}. The peak intensity was increased by ion doping. Futhermore, the peak intensity at ~1335 cm^{-1} decreases slightly because of graphitization by ion damage.

Figure 2 shows temperature dependent conductivity of n-type doped diamond films. The conductivity and activation energy of undoped film were 10^{-9} S/cm and 0.2 eV, respectively. The room temperature conductivity increases from ~10^{-9} S/cm to ~ 10^{-4} S/cm, and the activation energy drops from 0.2 eV to 0.1 eV by doping of 5.4×10^{15} cm^{-2} ion dose. By doping of 7.2×10^{16} cm^{-2} ion dose, the conductivity increases up to 5 S/cm and activation energy decreases down to 0.02 eV.

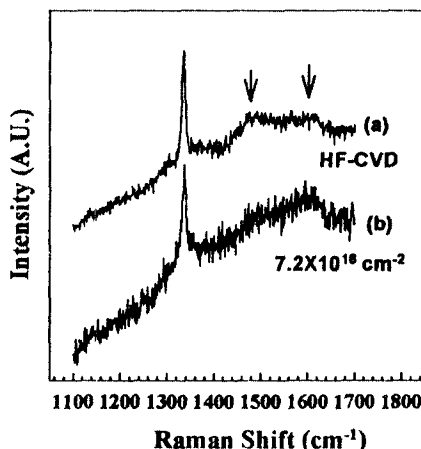


Fig. 1 Raman spectrum of undoped diamond films (a), and after n-type ion doping (b)

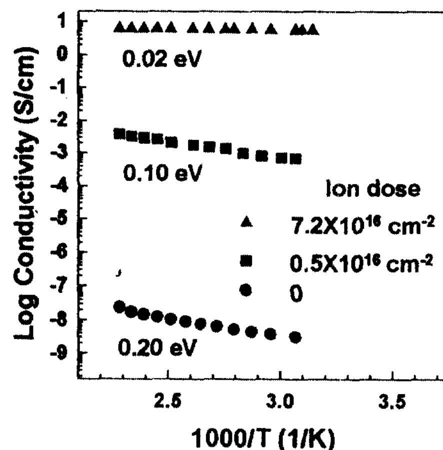
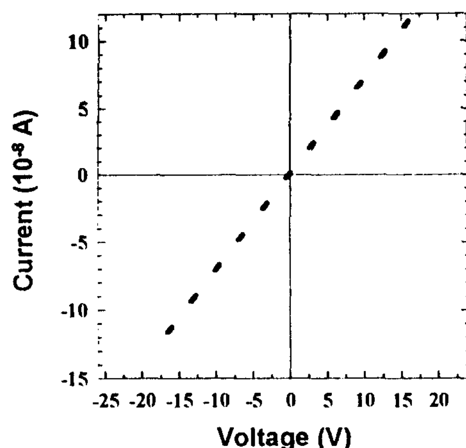


Fig. 2 Effect of ion doping on the temperature dependence of conductivity for diamond film



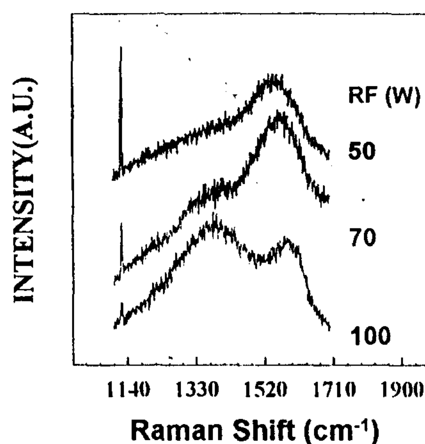


Fig. 3 Current-voltage (I-V) characteristics of n-type doped diamond film

Fig. 4 Raman spectra of DLC films deposited at various RF powers

Figure 3 shows current-votage characteristics of n-type doped diamond film. The characteristics shows linear current-voltage relation, showing ohmic behavior. This is believed to be due to tunneling through a thin depletion layer caused by heavy phosphorus doping in diamond[9].

3.2 Doping effect in DLC films

DLC films were deposited by a parallel-plate PECVD using $CH_4/H_2/He$ mixtures. The RF power and CH_4/H_2 flow rates were fixed at 100 W and 5 sccm, respectively. The self-bias potential, generated at the substrate holder, could remove weakly bonded C and H atoms in DLC films. The structural and electrical properties of hard DLC films strongly depend on deposition conditions such as gas flow rate and RF power. However, the deposited DLC films show nano-crystalline diamond peak at 1140 cm^{-1} [11] in additinal to the amorphous peaks at ~1350 cm^{-1} (D-peak) and ~1580 cm^{-1} (G-peak). The deposited films exhibited an optical band gap of ~1.3 eV, resistivity of ~10^{10} Ωcm, and hydrogen content of 18 at.%.

Figure 4 shows the Raman spectra for DLC films deposited at various RF powers using CH_4/H_2 (5 sccm). With increasing RF power, the peak intensity at 1350 cm^{-1} increases and the peak at 1140 cm^{-1} decreases.

Figure 5 shows the sheet resistance versus acceleration voltage for n-type doped DLC films. The doping temperature was fixed at 250 °C and acceleration voltage was varied from 6 kV to 20 kV with dose of 7×10^{16} atoms/cm^2. The sheet resistance decreases down to 2 kΩ/□ with increasing acceleration voltage, caused by increased depth of P in DLC films as well as more graphite fraction at the surface region. Compared to poly-Si by Excimer Laser annealing, sheet resistance decreases more rapidly with increasing acceleration voltage because of the graphization.

Figure 6 shows the sheet resistance versus ion dose for n-type doped DLC films at 250 °C. The acceleration voltage was fixed at 6 kV. The sheet resistance decreases down to about 6 kΩ/□ at ion dose of 3×10^{16} atoms/cm^2, and then saturates at higher dopings similar to poly-Si.

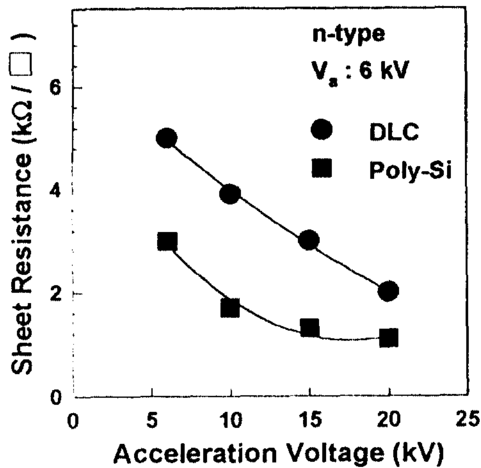


Fig. 5 Sheet resistance vs acceleration voltage for n-type doped DLC films

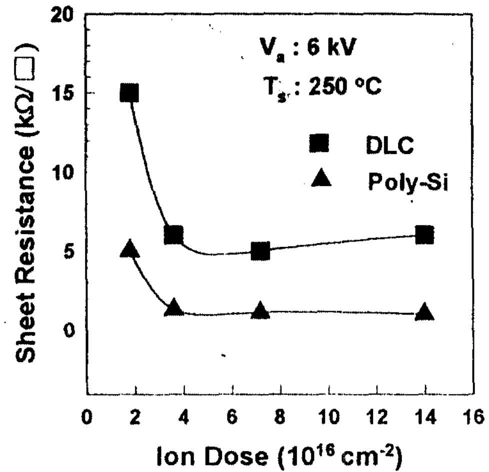


Fig. 6 Sheet resistance vs n-type ion dose for DLC films

Figure 7 shows the room temperature conductivity and activation energy of conductivity plotted against ion doping temperature. The acceleration voltage and ion dose (n-type) were fixed at 6 kV and 7×10^{16} atoms/cm^2, respectively. The conductivity increases with doping temperature, and the conductivity of 7 S/cm and activation energy of 30 meV were obtained at a doping temperature of 250 °C. The doping efficiency appears to increase with doping temperature.

Figure 8 shows the temperature dependence of dark conductivity for n-type DLC film doped with various ion doses. The conductivities of the doped DLC films have an activated form. The conductivity and activation energy of undoped DLC films were 10^{-10} S/cm and 0.3 eV, respectively. With increasing ion dose up to 7.2×10^{16} atoms/cm^2, the activation energy decreased down to 25 meV.

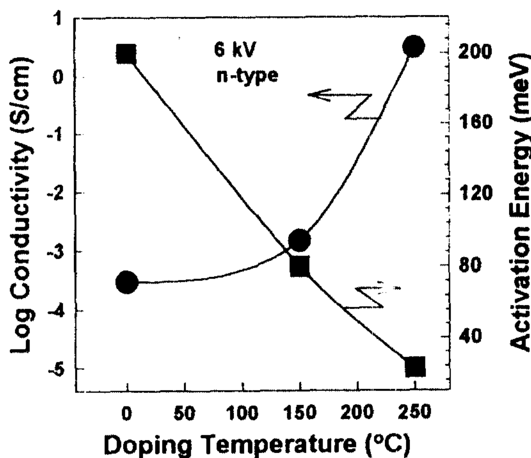


Fig. 7 Conductivity vs doping temperature for n-type ion doped DLC films

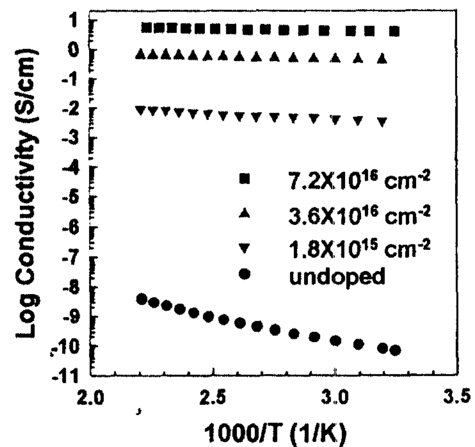


Fig. 8 Temperature dependence of conductivity for films doped with various ion doses

Figure 9 shows the sheet resistance versus ion dose for p-type DLC films doped at 250 °C. The acceleration voltage was fixed at 6 kV. The sheet resistance decreases down to about 16 kΩ/□ at 14×10^{16} /cm^2 ion dose.

Figure 10 shows the temperature dependence of the dark conductivity for the p-type DLC films doped with various ion doses. The maximum room temperature conductivity of 6×10^{-1} S/cm and minimum conductivity activation energy of 25 meV were obtained after ion doping of 1.4×10^{17} cm^{-2} ion dose.

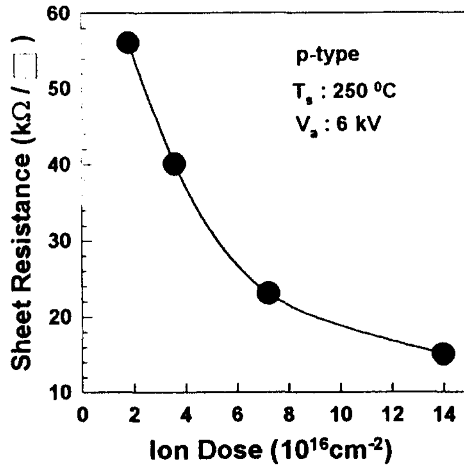


Fig. 9 Sheet resistance vs p-type ion dose for DLC films

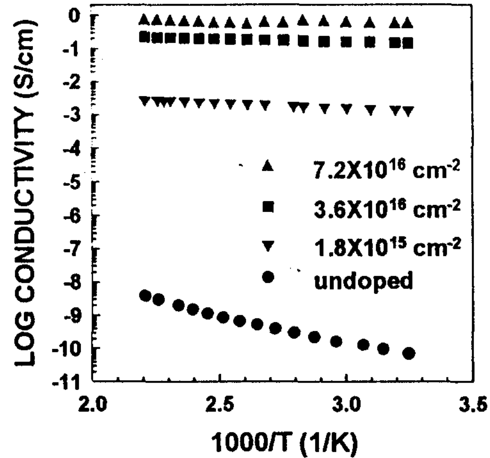


Fig. 10 Temperature dependence of conductivity for p-type ion doped DLC films

5. CONCLUSIONS

The doping effects on the electrical and structural properties of diamond films by HFCVD and DLC films by PECVD have been investigated. By PH_3 plasma ion doping in diamond films, maximun conductivity of 5 S/cm and minimum activation energy of 0.02 eV were obtained. The Raman intensity at 1330 cm^{-1} decreases slightly after doping of $\sim10^{16}$ ion dose. As for n-type doped DLC films, maximum conductivity of 7 S/cm and minimum conductivity activation energy of 30 meV were obtained. On the other hand, the maximum conductivity of 6×10^{-1} S/cm and minimum conductivity activation energy of 25 meV were obtained by p-type ion doping in DLC film.

6. REFERENCES

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