Vol 15 No 9, September 2006
1009-1963/2006/15(09)/2170-05

Chinese Physics

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and IOP Publishing Ltd

Electrical and structural properties of diamond films implanted by various doses of oxygen ions*

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(Received 14 January 2006; revised manuscript received 2 June 2006)

Oxygen-doped diamond films are prepared by implanting various dose oxygen ions into the diamond films synthesized by hot filament chemical vapour deposition, and their electrical and structural properties are investigated. Hall effect measurements show that lower dose oxygen ion implantation is beneficial to preparing n-type diamonds. The carrier concentration increases with the dose increasing, indicating that oxygen ions supply electrons to the diamonds. The results of AES spectrum indicate that oxygen ions are doped into the diamond films, and the O-implanted depth is around 0.1 μm. Raman spectrum measurements indicate that the lower dose oxygen ion implantation at 10^{14} cm^{-2} or 10^{15} cm^{-2} is favourable for producing less damaged O-doped diamond films.

Keywords: diamond films, n-type, oxygen, ion implantation
PACC: 8120V, 6170T

1. Introduction

The preparation of low resistivity n-type diamonds is still a difficult problem. Doping nitrogen,[1] phosphorus[2] or sulfur[3] into diamonds cannot achieve high conductivity n-type diamond films now. Oxygen may supply shallow donor energy levels in diamonds,[4] and it may introduce smaller distortion into diamonds than sulfur and phosphorus because of its smaller atomic radius. Therefore, oxygen may be a hopeful candidate for preparing n-type diamonds. It is well known that a large number of oxygen atoms participate in the chemical vapour deposition (CVD) growth of diamonds, but few oxygen atoms are found in diamonds, indicating very low solubility of oxygen in diamonds. Ion implantation is an important method to force the dopant into substrates, which has been applied to many materials, such as silicon[5] and GaN.[6] Ion implantation also can increase the solubility of oxygen in diamonds and realize oxygen doping in diamonds. Prins[4,7,8] investigated the oxygen doping in diamonds by ion implantation, and suggested that oxygen could supply shallow donor energy to the diamonds. However, he did not report on Hall effect results at room temperature and the temperature dependences of Hall effect parameters. Moreover, there exists no literature reporting on the influence of implantation dose on the electrical properties of the doped diamond films. In this paper, the electrical and structural properties of diamonds implanted by various doses of oxygen ions are investigated systematically by performing the Hall effect, AES and Raman spectra measurements.

2. Experiment

Most of ion implantations in diamonds are performed on single crystalline diamonds, otherwise grain boundaries and other CVD growth defects may give rise to detrimental effects on carrier mobility and on other electrical properties. Prawer *et al*[9] found that the change in resistivity of implanted diamond film was remarkably similar to that of the identically implanted diamond crystal, which suggests that the conduction mechanism in ion-beam-irradiated polycrystalline CVD diamond film is not mainly dominated by grain boundaries or graphitic impurities but determined by the intrinsic properties of diamond itself. Hence, the implantation and annealing procedures that are effective for the single crystal diamond should be applicable to polycrystalline CVD diamond

*Project supported by the Research Foundation of Education Bureau of Zhejiang province, China (Grant No 20050227).
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films[9]. Also, Kalish *et al*[10] found that CVD diamond doped by boron ion implantation yielded results comparable to those obtained for heavy B-doped polycrystalline diamond in the growth process. It is concluded that the doping of polycrystalline diamond by ion implantation is possible.[10] In addition, there are few reports on the investigations of oxygen ion implantation of CVD diamond films. Therefore, in this paper, we attempt to implant various doses of oxygen ions into the diamond films prepared by hot filament chemical vapour deposition (HF CVD) and study the electrical and structural properties of doped diamond films.

The intrinsic diamond films synthesized by HFCVD method on Si (111) were used as the substrates for ion implantation. The growth condition of diamond film was as follows: the carbon source was acetone, the volume ratio between acetone and hydrogen is 1%–2% with the total gas flow 200 ml/min, the working pressure in the reaction chamber was 0.5–1.4 kPa, and the temperature of the substrate was about 850°C. Raman spectroscopy and x-ray diffraction (XRD) measurements indicated that the synthesized diamond films were pure and of high quality. The ion implantation was performed on the 100 keV isotopic separator at room temperature. The ion energy was 90 keV, and the doses are listed in Table 1. The carbon ion implantation was used as the contrast of oxygen ion implantation. All the samples were implanted at the same dose rate $3\,\mu A\cdot cm^{-2}$. As the first step, samples O14 were annealed in a wide temperature range in order to choose an appropriate annealing temperature range for other implanted films. Samples O14 were annealed at 500, 650, 800, 900 and 1000°C for 30 min in an Ar-protecting atmosphere, and the annealing properties were first investigated by the relationship between the resistivity of the samples and the annealing temperature.

Table 1. The doses of oxygen and carbon ion implantation.

Samples	Dose/cm^{-2}
O14	1×10^{14}
O514	5×10^{14}
O15	1×10^{15}
O16	1×10^{16}
C15	1×10^{15}

The annealed samples were boiled in an acid mixture of H_2SO_4/H_2O_2=1/1 for 5 min followed by their rinsing in deionized water. Ti (500 nm) / Au (500 nm) contacts were made and then annealed in vacuum at 450°C for 20 min as the electrical probes. Hall measurements by the van der Pauw method were performed at room temperature and also in the temperature range of 200–450 K in vacuum by using the Accent HL550 Hall system. Auger emission spectroscopy (AES) measurement was performed by using PHI550ESCA/SAM. Ar ion current density was 170 $\mu A/cm^2$, and the scan rate was 17 nm/min. The voltage of primary electron beam (E_p) was 3 keV, and the current of primary electron beam (I_p) was 1 μA. Ar ion etching voltage (V_I) was 3 kV, and the Ar ion current density (I_I) was 170 $\mu A/cm^2$. The background pressure is 1.3×10^{-8}Pa and working pressure was 2.7×10^{-5}Pa in Ar atmosphere. The Raman measurements were performed on the Lab RAM HRUV80C, and the wavelength was 632.8 nm.

3. Results and discussion

Figure 1 shows the dependence of the resistivity of sample O14 on the annealing temperature, measured by two-probe and ZC36 high resistance meter. It is shown that the resistivity is high under 500°C and 650°C annealings and then decreases with annealing temperature increasing up to 800°C, indicating that the annealing changes the electrical properties of oxygen ion implanted diamond and lower energy band may be formed. When the annealing temperature is over 900°C, the resistivity increases again. This result is in accordance with that of Prins,[4] and he suggested that the donors in oxygen implanted diamond could be more complex and the simplest alternative possibility was an oxygen interstitial trapped at a vacancy. In our experiment, the annealing temperatures were chosen as 800, 900 and 1000°C for other samples.

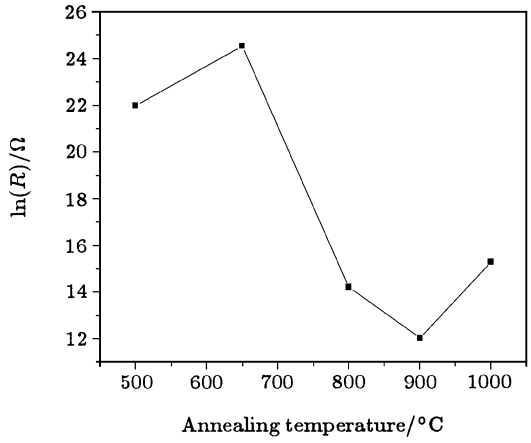


Fig.1. The dependence of normalized resistance of sample O14 on the annealing temperature.

Table 2 lists the Hall effect measurements at room temperature of samples annealed at 900°C. It is seen that all the samples implanted by oxygen ions are of n-type conduction, and the conduction of the sample implanted by carbon ion is of p-type. It is revealed that the influence of oxygen ion implantation on the electrical properties of the implanted diamond is different from that of C-ion implantation, and oxygen may supply electrons in the diamond film. For the sample whose conduction is from the defect, there are no Hall effects that can be measured at any temperatures due to very low carrier mobility.[11] However, in our experiment, the Hall mobility and carrier concentration are measured at room temperature, and the resistivity is not very high. These results indicate that the electrical conduction of O-doped diamond originates from not only the defect produced by ion implantation but also the oxygen ions. Hall effect values of the samples at room temperature are not obtained from relevant publications.[4,7] In addition, the resistivity of the samples basically decreases with the implantation dose of oxygen ion increasing, while the carrier concentration increases with the dose increasing. It is stated that oxygen can supply electrons to diamond and it may be a donor dopant for diamond.

Table 2. The values of Hall effect of the samples annealed at 900°C.

Sample	$\rho/\Omega\cdot$cm)	$R_{\rm H}/({\rm m}^2/{\rm C})$	$\mu_{\rm n}/({\rm cm}^2\cdot{\rm V}^{-1}\cdot{\rm s}^{-1})$	$n/{\rm cm}^3$
O14	25.19	–71.8	11.4	2.17×10^{16}
O514	32.34	–2.06	0.25	7.58×10^{17}
O15	4.566	–1.95	1.71	8.01×10^{17}
O16	0.03055	–0.0399	5.23	2.28×10^{18}
C15	4.04	0.52	0.482	2.53×10^{18}

To thoroughly investigate the electrical properties of O-doped diamond, we measured the temperature dependence of the resistivity as shown in Fig.2. The plot of $\ln\rho$ vs $1/T$ follows a linear dependence, indicating a thermally activated behaviour of the conductivity. In the whole temperature range, the Hall coefficient is always negative, revealing n-type conduction of the samples.

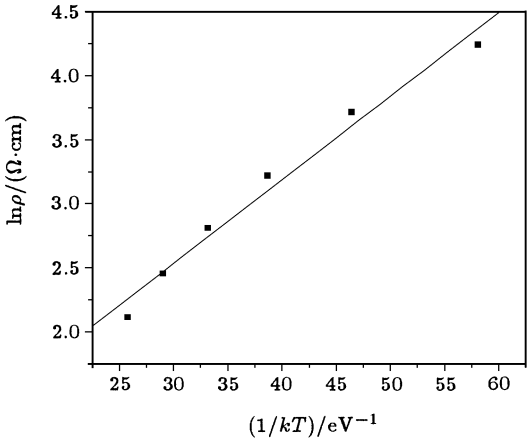


Fig.2. The resistivity of sample O14800 as a function of temperatures.

Figure 3 shows the Raman spectra of the samples O14, O15, O16, and C15. It is seen that the finger peak of diamond of $1332\,{\rm cm}^{-1}$ has nearly no shift in the samples O14 and O15, and a broad scatter peak at $1540\,{\rm cm}^{-1}$ can be found, which corresponds to the amorphous diamond. The G peak related to $1580\,{\rm cm}^{-1}$ is not found in their Raman spectra. When the oxygen ion implantation dose increases up to $10^{16}\,{\rm cm}^{-2}$, the diamond finger peak is broadened and a stronger peak at $1590\,{\rm cm}^{-1}$ can be found, whose structure is the same as that of the carbon black. It is revealed that the diamond film is damaged heavily by $10^{16}\,{\rm cm}^{-2}$ oxygen ion implantation, and the critical implantation dose of oxygen ion is $10^{16}\,{\rm cm}^{-2}$. The oxygen doping in diamond must be performed below $10^{16}\,{\rm cm}^{-2}$ in the further investigation. The change in structure of implanted diamond by oxygen is similar to that of implanted diamond by nitrogen.[12] In addition, a prominent peak at $1562\,{\rm cm}^{-1}$ for sample C15 can be found, which is close to the G band. It is indicated that the graphite phase is produced in diamond implanted by carbon ion. However, the peak at about $1540\,{\rm cm}^{-1}$ in sample O14 or O15 is not found, indicating that the structure of diamond implanted by oxygen ion is different from that by carbon ions. The lower dose oxygen ion implantation at $10^{14}\,{\rm cm}^{-2}$ or $10^{15}\,{\rm cm}^{-2}$ is beneficial to obtaining n-type diamonds with less lattice damage in the present experiment.

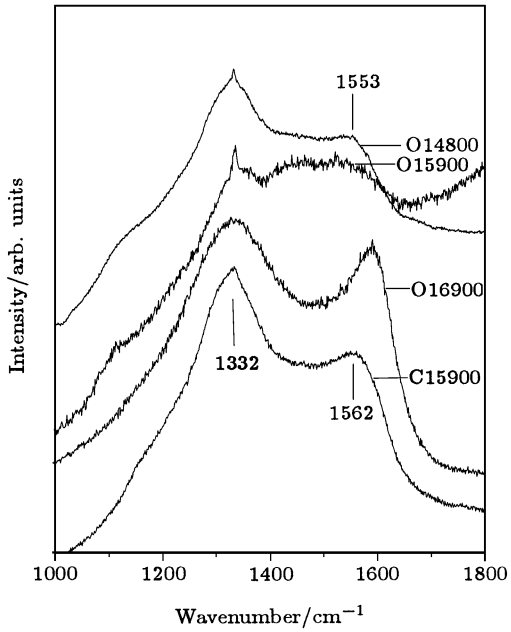


Fig.3. The Raman spectra of samples O14, O15, O16 and C15.

Figure 4 shows the AES spectrum and peeling test of the samples, from which we can obtain the compositions and the distribution of oxygen ions in diamond films. In Fig.4(a), the distinct absorption peaks can be found at 272 eV and 503 eV, which correspond to carbon and oxygen respectively. It reveals that oxygen ions are already doped into diamond films by implantation. Other compositions are not found by using the spectroscopy, displaying the high purity of O-doped diamond films. Figure 4(b) shows the relation between the time and the concentration of oxygen ions, indicating the variation in the concentration of oxygen ion with the film depth. Three zones can be found in Fig.4(b). The first zone ranges from 0 to 10 nm; oxygen concentration increases with the increase of depth. The second zone is in the 10 to 45 nm range, oxygen concentration changes in a small range. The third is in a range from 45 to 80 nm, oxygen concentration deceases compared with that in the second zone. And then the oxygen ion concentration decreases down to zero quickly. From the above analysis, the second zone may be the averaged projection range of oxygen ion in diamonds,[13] and the diffusion of oxygen ions in the high temperature annealing process may be helpful for producing the third zone. The result reveals that the oxygen ion implantation is about 0.1 μm in depth.

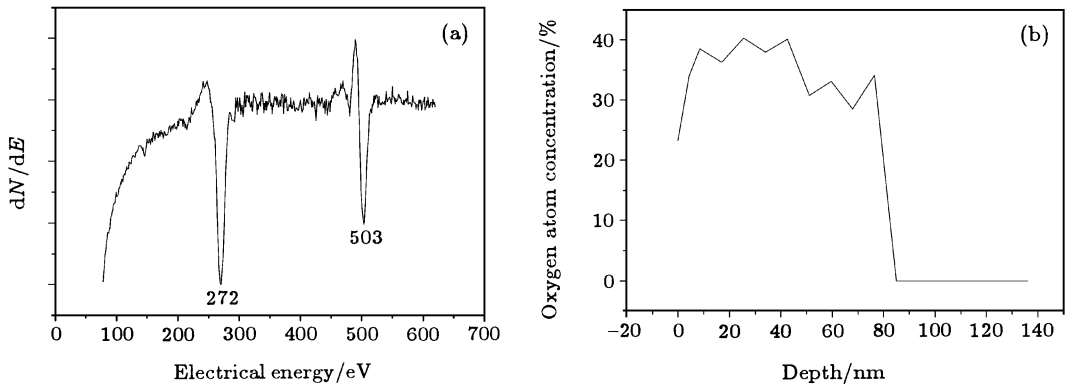


Fig.4. (a) AES spectrum of the surface of sample O14 annealed at 900°C, (b) The variation in oxygen atom concentration with film depth of sample O14 annealed at 900°C.

4. Conclusions

The oxygen-doped diamond films are prepared by various dose oxygen ion implantation. Hall effect measurements show that oxygen ion implantation is beneficial to obtaining n-type diamonds. The carrier concentration increases with the dose increasing, indicating that oxygen ions supply electrons to the diamond films. The AES spectrum indicates that oxygen ions are doped into the diamond film, and the thickness of O-doped diamond is around 0.1μm. Raman spectrum measurement displays that the microstructure of the diamond film implanted by oxygen ion is different from that by carbon ion. The lower dose oxygen ion implantation at 10^{14} cm^{-2} or 10^{15} cm^{-2} is favourable for achieving less damaged O-doped diamond films in the present experiment.

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