The electrical properties of sulfur-implanted cubic boron nitride thin films*

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Cubic boron nitride (c-BN) thin films are deposited on p-type Si wafers using radio frequency (RF) sputtering and then doped by implanting S ions. The implantation energy of the ions is 19 keV, and the implantation dose is between 10^{15} ions/cm^2 and 10^{16} ions/cm^2. The doped c-BN thin films are then annealed at a temperature between 400 °C and 800 °C. The results show that the surface resistivity of doped and annealed c-BN thin films is lowered by two to three orders, and the activation energy of c-BN thin films is 0.18 eV.

Keywords: cubic boron nitride, ion implantation, surface resistivity, activation energy

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1. Introduction

Cubic boron nitride (c-BN) has drawn considerable attention because its excellent physical and chemical properties are comparatively close to those of diamond. c-BN, as well as diamond, has extreme hardness, high chemical stability, a wide band-gap ($E_g \approx 6$ eV), and large thermal conductivity. Furthermore, c-BN is superior to diamond in cutting tools applications due to its chemical stability without any thermal reaction during the machining of ferrous materials. Diamond is more limited in cutting tools because of its strong carbide formation reaction with ferrous elements. As a kind of semiconductor material, c-BN can be easily doped as an n or p type and has a very high breakdown voltage. Therefore, c-BN is considered as a promising wide band-gap III–V semiconductor suitable for high power transistors and opto-electronic devices.

The doping and electrical properties of c-BN films are the basis of studying their applications in microelectronics. In 1962, Wentorf[1] added Be (metal or salt) with a weight ratio between 0.01% and 1% into the synthetic system, synthesized p-type semiconductor material at high pressure and estimated the activation energy at 0.19 eV∼0.23 eV.

In the present article, we report on the n-type doping of c-BN films by S ion implantation. To date, there have been few studies on the S ion implantation of c-BN films and the activation energy of S-doped c-BN films.

2. Experiment

c-BN thin films were deposited on p-type Si wafers using RF sputtering and doped by implanting S ions. The films were characterized by Fourier transform infrared (FTIR) spectroscopy with a WQF–310 spectrometer, and the thickness of the film was measured by the Veeco Dektak-150 surface profile measuring system to be about 400 nm. The ion implantation energy was 190 keV, and the implantation dose was between 10^{15} ions/cm^2 and 10^{16} ions/cm^2. The high temperature vacuum annealing method was used to activate the doped c-BN thin films. The vacuum pressure was 2 Pa, the annealing temperature was between 400 °C and 800 °C, and the annealing time was 60 min. An aluminum (Al) layer was deposited on the film with a 2 mm×5 mm area by the vacuum evaporation method, and the surface resistivity was measured with a Keithley 6517 electrometer. In order

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to measure the conductivity activation energy, we also used the high resistance meter to measure the voltage and the current of the films at temperatures ranging from 290 K to 363 K. By calculating the thin film resistance, we obtained the variation in the conductivity of the samples with temperature, so that the activation energy could be calculated.

3. Results and discussion

3.1. Surface resistivity of the BN film

Figure 1 shows the IR spectra of the c-BN film before and after S ion implantation at a dose of 5×10^{15} ions/cm^2. From the spectra, it can be seen that the full width at half maximum (FWHM) values of the c-BN and h-BN peaks both become wider after S ion implantation. This indicates that the c-BN film crystalline becomes worse after S ion implantation.

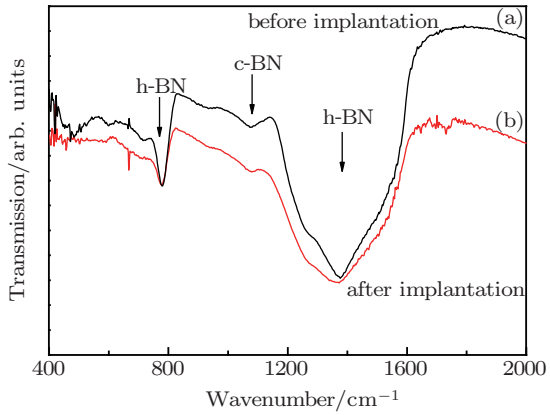


Fig. 1. (colour online) The IR spectra of the c-BN film before (a) and after (b) S ion implantation.

The surface resistivity of the c-BN film before S ion implantation is 1.8×10^{11} Ω·cm. It is changed significantly after S ion implantation and annealing. As the annealing temperature and the dose of S ions increase, the resistivity decreases. Table 1 shows that after annealing at 400 °C, the surface resistivity changes with implantation dose. As can be seen from the table, the resistivity of the S-doped c-BN film after annealing at 400 °C is reduced by about 2∼3 orders of magnitude compared with that without S ion implantation.

Table 1. The surface resistivities of BN films doped by ion implantation with different ion doses.

Dose/(ions/cm^2)	Resistivity/Ω·cm
0	1.80×10^{11}
10^{15}	5.07×10^{9}
5×10^{15}	3.62×10^{9}
10^{16}	1.61×10^{8}

The curve was drawn using the data in Table 1, and is shown in Fig. 2. It can be seen from the figure that the resistivity of the c-BN film after ion implantation changes greatly compared with that before implantation. And the resistivity of the doped c-BN film does not vary significantly with implantation dose.

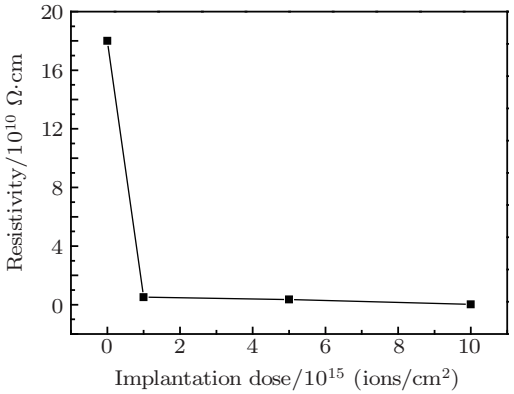


Fig. 2. The surface resistivity of the BN film versus the implantation doses.

3.2. Conductivity activation energy of the BN film

The c-BN film usually has a typically amorphous structure. According to the Mott-CFO model,[2,3] there are four electronic conduction mechanisms of amorphous semiconductors, i.e., the conductivity in the extended states, the conductivity in the tail of localized states, the conductivity in the band-gap defect of localized states, and the conductivity in the band gap of localized states in a variable range hopping system. The relation between total conductivity and temperature can be expressed as follows:[3–5]

$$\sigma = \sigma_0 \mathrm{e}^{-E/kT} + \sigma_1 \mathrm{e}^{-E_1/kT} + \sigma_2 \mathrm{e}^{-E_2/kT} + \sigma_3 \mathrm{e}^{-A/kT^{1/4}},$$

where $\sigma_0 \mathrm{e}^{-E/kT}$ is the conductivity in the extended state, $\sigma_1 \mathrm{e}^{-E_1/kT}$ is the conductivity in the localized band tail states, $\sigma_2 \mathrm{e}^{-E_2/kT}$ is the conductivity in the defect states in the band gap, and $\sigma_3 \mathrm{e}^{-A/kT^{1/4}}$ is the conductivity in the band gap of localized states in a variable range hopping system. These conduction mechanisms of the material do not work at the same time. Which conduction mechanism works at a definite temperature depends on the relationships among the various parameters.

For the sample implanted with an ion dose of 5×10^{15} ions/cm^2, we use the high resistance meter and the variable temperature system to measure the temperature dependence of the resistivity of the S-implanted BN film in a temperature range from 290 K to 363 K. Then the conductivity is calculated. Figure

3 shows the linear fitting relationship between $\ln\sigma$ and $1/T$. In the temperature range of 290 K–363 K, we obtain an activation energy of 0.18 eV from the slope of the straight line.

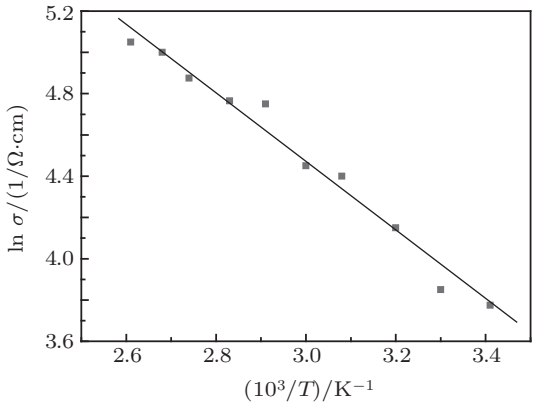


Fig. 3. The temperature dependence of the resistivity of the BN film.

BN is a wide band-gap semiconductor material whose band gap is about 6 eV. Its activation energy corresponding to the extended state and that corresponding to the localized band tail state are of the same order of magnitude as the band gap. The variable range hopping conductivity usually appears at very low temperatures. Therefore it can be concluded that the activation energy of 0.18 eV is that of the implanted sulfur defect state in the band gap of the BN film.

The activation energy of S-doped BN films has not been reported up to now as far as we know. In Ref. [1] the activation energy of Be-doped BN films was reported to be 0.19 eV∼0.23 eV. In Ref. [6] the activation energy of Si-doped BN films was given to be 0.24 eV. In Ref. [7] the activation energy of Be-doped BN films was found to be 0.20 eV. The conductivity activation energy of the S-doped BN films we obtained here is very close to those reported in the references.

4. Conclusions

BN thin films are deposited using RF sputtering, and doped by implanting S ions. The resistivity is found to be reduced by 2∼3 orders of magnitude after implanting and annealing. Conductivity measurements are carried out in a temperature range of 290 K–363 K. According to the relationship between conductivity and temperature, the activation energy is calculated to be 0.18 eV.

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