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EFFECT OF O^+ ION BEAM ON THE ELECTRICAL CONDUCTION OF CARBON FILMS BY IBSD TECHNIQUE

by

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ABSTRACT

Carbon films were deposited by sputtering a graphite target with Xe^+ ion beam. During deposition, an additional low-energy ion beam, composed of O^+ ions and Ar^+ ions, was irradiated on the growing layers. The resistivity of the films was found to decrease with increasing relative concentrations of O^+ ions against Ar^+ ions and against carbon atoms. It was also found that scarce oxygen atoms were observed in the films by irradiating O^+ ions. The variable hopping conduction model was found to be applicable to describe the temperature dependence of the film resistivity for all specimens studied with temperatures of two; i.e. lower than 50 K and higher than 50 K. Furthermore, density of hopping sites increased with increasing relative concentration of O^+ ions. Some discussions such as mechanism of hopping sites in the film and work of oxygen during deposition were also expressed.

Introduction

There are many techniques to make films in non-equilibrium state, for example ion beam sputtering, low-energy ion beam deposition, ion plating, rf sputtering, magnetron sputtering and so forth. There is no commonly accepted argument on the structure of so-called amorphous carbon films made by such methods, though all of the workers agree that the carbon bonding inside the film should be a mixture of trigonal (sp^2) and tetrahedral (sp^3) one mainly. Since both of them constitute graphite and diamond bonds respectively, the electrical conduction mechanism of the film depends on the types of the mentioned bondings (Hauser 1977).

Accoring to the three dimensional variable range hopping model for non-crystalline materials, the electrical resistivity ρ, against temperature T, is written as

$$\rho \propto \exp(B/T)^{1/n} \tag{1}$$

and

$$B=\frac{\alpha^3}{K_B N(E_F)} \tag{2}$$

where α^{-1}, K_B, and $N(E_F)$ represent the decay length of the localized wave function, Boltzmann's constant, and the density of localized states, respectively. In equation (1), $n=4$ (Mott 1969), while in two-dimensional problems, 3 replaces 4 (Hamilton 1972). Taking into account Coulomb interaction between electrons, $n=2$ has been obtained at low temperatures, both in three and in two dimensions (Efros and Shklovskii 1975).

The carbon films grown by the IBSD (ion beam sputtering deposition) are expected to have fewer impurities than those grown by other deposition techniques, because the deposition is carried out under the lower pressures. By the use of IBSD method, furthermore, microstructures of the films may be easily controlled by changing deposition conditions such as ion beam accelerating voltage and current. Electrical properties of the carbon films manufactured by IBSD have been examined, however, detailed examinations concerning to mentioned model was not done as yet (Ohashi and Masaki 1992, Ise and Ohashi 1993).

Now, it seems that only the strongly bonded carbons should compose the film when O^+ ions are irradiated additionally on the depositing film during IBSD, since O^+ ions are supposed to reach with carbon atoms on the film surface and then to make carbon mono- and/or di-oxide gaseous molecules. Thus the microstructure or the microscopic state of carbon bonding in the film may be controlled by varying the density of O^+ ions added during the film deposition.

With these considerations in mind, we manufactured carbon films by IBSD technique with additional O^+ ions irradiated on the growing films. The temperature dependent electric conduction as well as microstructure of the carbon films were examined in relation with the concentration of O^+ and Ar^+ ions during deposition.

Experimental

IBSD system

An ion beam sputtering deposition system used for preparing carbon films is shown in Fig. 1. Fundamentally, the system was composed of two Kaufman-type double grid ion sources (IONTECH. INC) and a deposition chamber, which was evacuated by a cryopump to a base pressure of 2×10^{-6} Torr, and was kept 2×10^{-4} Torr during deposition.

The ion source *1* (5 cm in diameter) produced 1200 eV Xe^+ ions in order to sputter a graphite target and then sputtered carbon atoms were deposited on substrates. We used pure xenon as a sputtering gas instead of commonly used argon, because the sputtering yield of a Xe^+ ion is higher than that of an Ar^+. The ion source *2* (15 cm in diameter) generated a mixture of 200 eV O^+ and Ar^+ ions. The ion beam of these mixed ions was irradiated directly on the growing layer during deposition. By the operation of the ion source *2* with the mixture of argon and oxygen, the ion beam was kept stable. The ion source *2* without argon, however, ceased generating the ion beam since oxygen atoms oxidise the inner wall of the ion

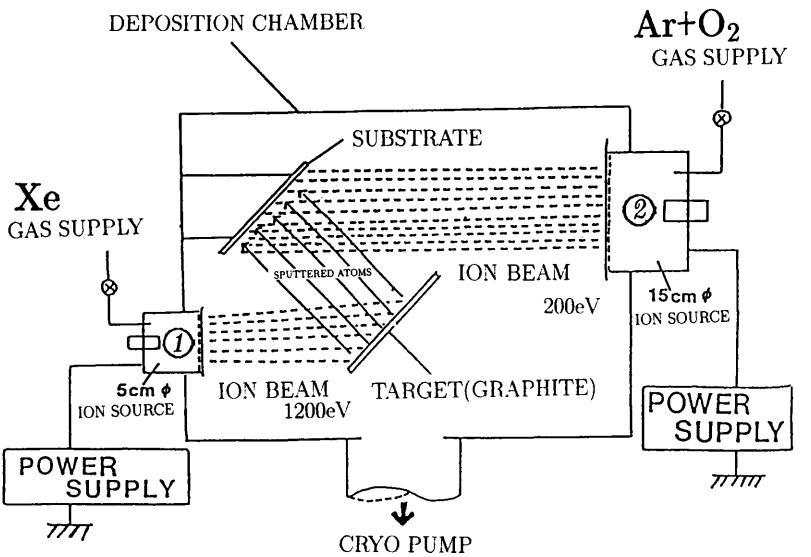

Fig. 1. Shematic diagram of IBSD apparatus.

source *2*. In the deposition chamber, a high purity graphite target (30 cm in diameter) including less than 20 ppm impurities was mounted about 20 cm apart from the ion source *1*, and the target was located at a distance of 7 cm from the substrate holder facing each other. The distance between the substrate holder and ion source *2* was about 40 cm. The locations of ion sources *1* and *2* were taken into account lest the ion beams irradiated from these two ion sources should interrupt with each other. The beam power of ion source *1* varied between 50 and 150 W under a voltage of 1200 V, and oxygen gas flow to ion source *2* varied between 0 and 0.5 SCCM (cc/minute in standard state). During deposition, xenon gas flow to ion source *1*, and argon gas flow to ion source *2* were held at values between 2.2 and 5.0 SCCM, respectively. Before deposition, the substrates were cleaned in the deposition chamber by Ar^+ ion beam irradiation of energy 200 eV with current 50 mA for 2 minutes. The substrate holder was connected to an earth terminal for discharge. A series of films were grown on various substrates: silicon wafers for XPS (X-ray photoelectron spectroscopy) analysis, KBr single crystals for TEM (transmission electron microscopy), and fused quartz plates for electrical measurement. The resistivity of these films was found not to depend on the thickness conspiciously at room temperature and the deposition was carried out so that each film has a thickness ranging from 800 to 1200 A (Ohashi and Masaki 1987).

Measurement

The planar resistance of the film was obtained by an electrometer. The measurement was carried out in the ohmic region i.e. current density of approximately 100 A/cm^2 at room temperature and a fixed applied voltage. The temperature dependence of the resistivity was measured between room and liquid helium tem-

peratures. The temperature was monitored with Au–Fe/chromel thermocouple.

The carbon films deposited on silicon wafers were analysed using XPS. XPS measurements were performed with etching treatment for the depth profile, in order to determine the oxygen content both at the surface and inside the film. The carbon films deposited on KBr substrates were floated off onto copper grids by dissolving the substrates into 50% aqueous solution of ethyl alcohol, and were examined by TEM with an electron accelerating voltage of 200 kV.

Results and Discussion

Oxygen profiles by XPS across the deposited film in Fig. 2 show that scarce oxygen does exist inside the film irrespective of concentration of irradiating O^+ ions during sputtering. Characteristics in Fig. 2 may be understood assuming that almost all the O^+ ions contribute to form oxygen-carbon compounds in gaseous state during the film formation process as described already in "Introduction".

Fig. 3 and Fig. 4 show electron micrographs for films deposited with sputtering Xe^+ beam power of 150 and 60 W, where scarce morphological difference was recognized.

Fig. 5 shows the resistivity of specimens deposited under conditions with and without mixed ($Ar^+ + O^+$) ion beam irradiation vs. sputtering (Xe^+) ion beam power at room temperature. Mixed ion beam irradiation raises the resistivity of carbon films for Xe^+ ion beam power of our measurement, and the film resistivity under irradiation of mixed ion beam decreases with decreasing Xe^+ ion beam power. In Fig. 5 the decrease in Xe^+ ion beam power corresponds to the increase in relative concentration of O^+ ions against carbon atoms deposited on the film surface.

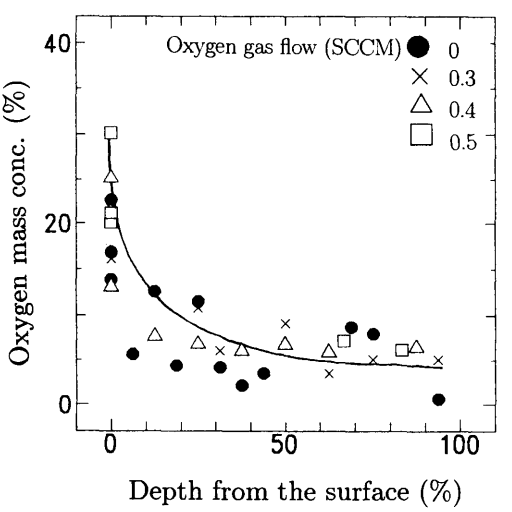

Fig. 2. XPS depth profile of oxygen concentration for various oxygen gas flow. In the figure, 100 (%) of depth from the surface means bottom of the film.

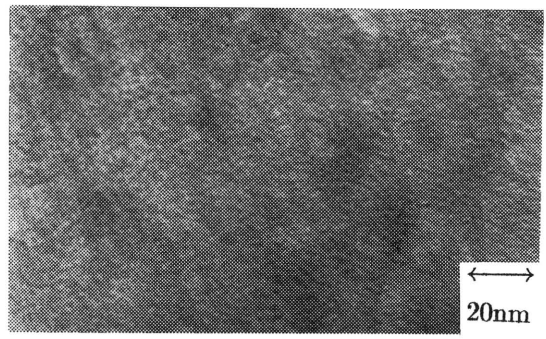

Fig. 3. TEM image of the sample film deposited with sputtering power of 150 W.

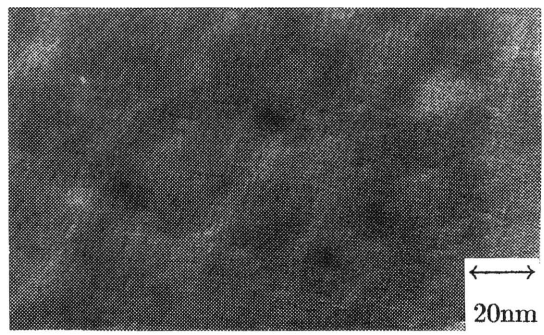

Fig. 4. TEM image of the sample film deposited with sputtering power of 60 W. Comparison of Figs. 3 and 4, see context.

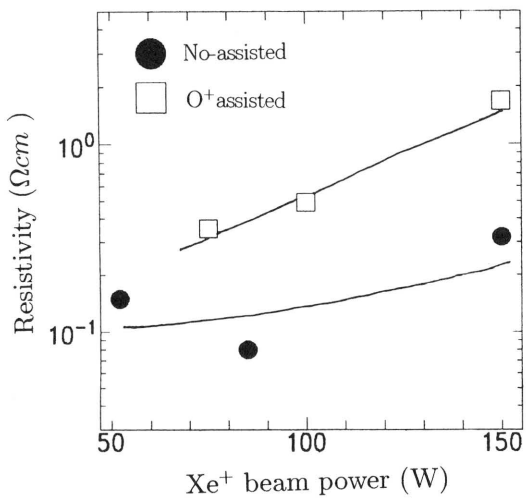

Fig. 5. Resistivity vs. Xe^+ beam power. The amount of oxygen gas flow for O^+ assisted samples is 0.3 SCCM.

Fig. 6 shows the resistivity and deposition rate vs. oxygen gas flow, where zero oxygen flow corresponds to the lack of mixed ion beam from ion source *2* in Fig. 1. Clearly, the resistivity of the films decreases with increasing oxygen gas flow. Consequently, amount of O^+ ions are found effective to decrease the film resistivity, and at the same time that of Ar^+ ions have an effect on increasing resistivity, since increase in O^+ flow means decrease in relative concentration of Ar^+ ions. The tendency that deposition rate decreases with increasing oxygen gas flow seems to support the assumption that O^+ ions combine with carbon atoms to be removed from film surface. Similarly the film resistivity and deposition rate increase with increasing sputtering

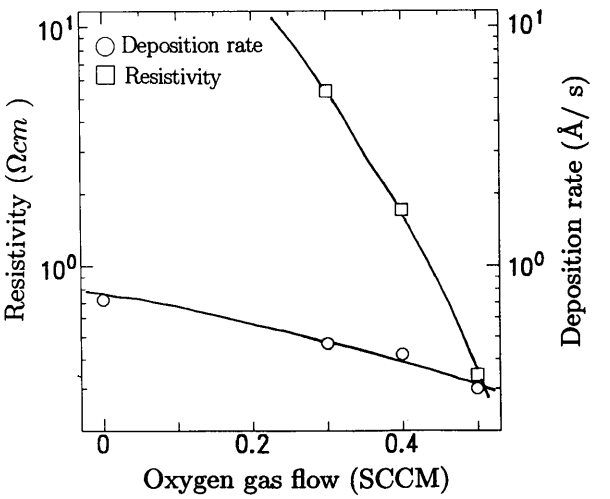

Fig. 6. Resistivity and deposition rate as a function of oxygen gas flow.

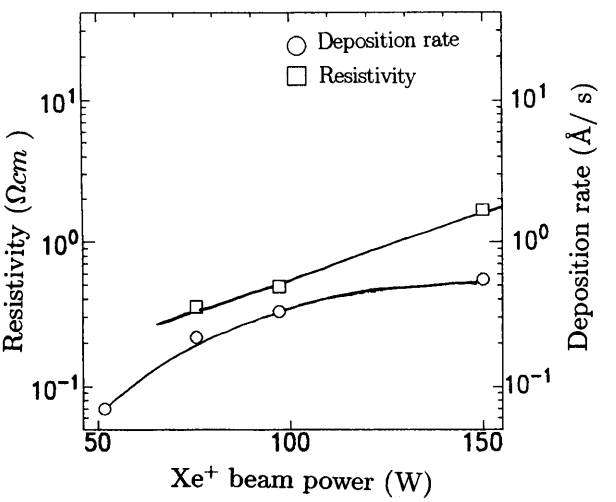

Fig. 7. Resistivity and deposition rate as a function of Xe^+ beam power.

Xe^+ ion beam power (see Fig. 7). These behaviours may be understood by taking into account the mentioned discussions that the increase in Xe^+ ions means the decrease relative content of O^+ ions.

Fig. 8 shows the temperature dependence of the resistivity for various oxygen gas flow, and Fig. 9, for various sputtering Xe^+ ion beam power. As is written in 'Introduction', the variable range hopping model known as a conduction model of amorphous materials can be applicable to amorphous semiconductors. The

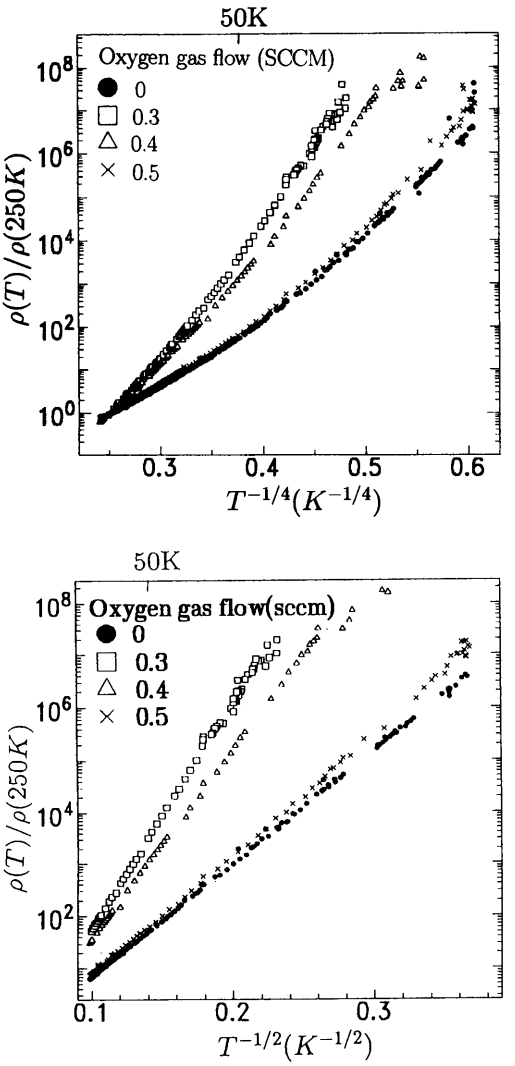

Fig. 8. Resistivity, ρ, vs. temperature, T, for various oxygen gas flow under the conditions of argon gas flow, 5 SCCM and Xe^+ beam power, 150 W. Fig. 8a shows ρ vs. $T^{-1/4}$, and Fig. 8b, ρ vs. $T^{-1/2}$.

temperature dependent resistivity of amorphous germanium has been shown to be described by equation (1) with $n=4$ for over a wide temperature range (between 10 K and room temperature) (Pollak, Knotek, Kurtzman and Glick 1973). Whereas, our results showed different n values above and below critical temperature $T_c=50$ K, i.e. $n=4$ at $T_c>50$ K (see Figs. 8a and 9a), and $n=2$ at $T_c<50$ K (as shown in Figs. 8b and 9b). It is naturally expected that the conduction mechanism differs above and below T_c. It should be noted that T_c is the same for all of our specimens studied,

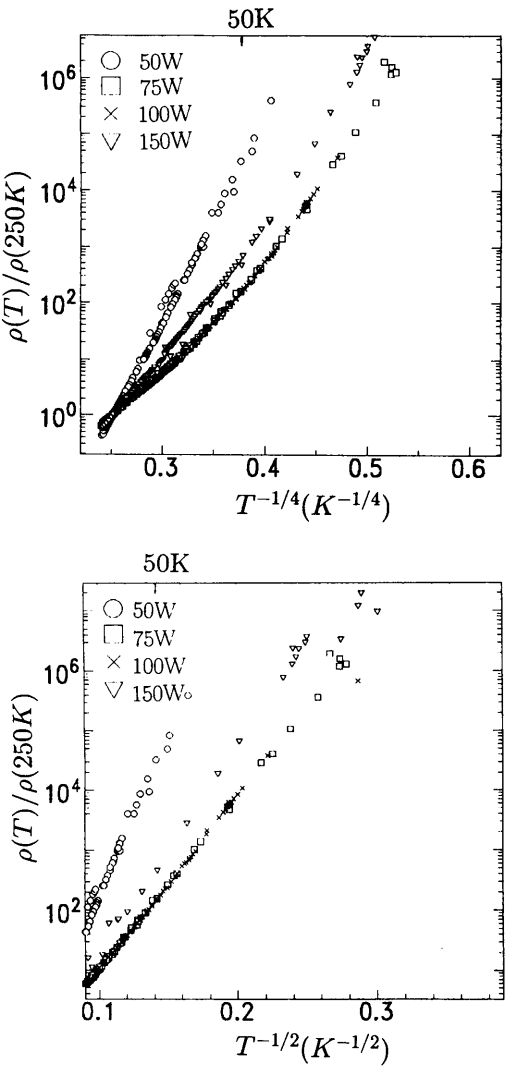

Fig. 9. Resistivity vs. temperature for various sputtering Xe^+ beam power under the condition of oxygen gas flow, 0.3 SCCM. Fig. 9a indicates ρ vs. $T^{-1/4}$, and Fig. 9b, ρ vs. $T^{-1/2}$.

though the magnitude of B in equation (1), determined from the results in Figs. 8 and 9, decreases with increasing O^+ ion concentration. Considering expression of B in equation (2), we may assume that B decreases with increasing density of hopping sites, $N(E_F)$, if the decay length of the localized wave function, α^{-1}, is supposed to be unchanged. The hopping sites may be originated from trigonal bonding. It may thus be concluded that the effect of the irradiation of O^+ ions is to remove carbon atoms weakly connected with each other from the film surface and to increase the number of trigonally bonded carbons which acts as hopping sites. In this study, we use Ar^+ ion as a carrier gas of O^+ ions. Further detailed investigations concerning the influence of carrier Ar^+ ions during deposition will be necessary to clarify the detailed electrical conduction mechanisms of the film.

Conclusion

Cabon films were deposited by IBSD tequnique. During deposition, the irradiation of additional low energy O^+ ion beam on the growing film surface reduced the resistivity of the films. Temperature dependence of the resistivity shows that the variable range hopping conduction model can be applicable with two temperature regions i.e. the results can be described by equation (1) with $n=4$ for $T_c > 50\,\mathrm{K}$ and $n=2$, $T_c < 50\,\mathrm{K}$. The irradiation of O^+ ion beam during the film formation may have an effect to increase hopping sites of the carbon film.

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