ION IMPLANTATION OF DIAMOND-LIKE CARBON FILMS

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ABSTRACT

Diamond-like carbon (DLC) films (a-C:H) were implanted by 140 keV and 110 keV Ar ion beams. The resistivities of the implanted films decreased dramatically under a dose of 2×10^{16} Ar/cm^2. IR spectra and optical gap E_{opt} were measured. It was found that the sp^2 and sp^3 components decreased due to the loss of hydrogen during implantation, and the ratio of components sp^2 bonds to sp^3 bonds increased with the ion dose. And the optical gap E_{opt} decreased from 1.46 eV to 0.83 eV. The hydrogen (bonded and unbonded) contents in the films were measured with the nuclear resonant reaction ^{1}H(^{19}F, $\alpha\gamma$)^{16}O. It is shown that hydrogen plays an important role in affecting some properties of DLC fims.

Keywords: Ion implantation Diamond-like film

1 INTRODUCTION

Diamond-like carbon (DLC) films have been studied in recent years because of their very attractive properties such as extreme hardness, transparency to IR radiation, variable electrical characteristics, chemical inertness and so on[1-3]. Up to now, however, the relation between structures and properties of DLC films is still not quite clear[4].

F.W.Smith reported the graphitic (sp^2) component grows with annealing at above 450°C[5]. S.Prawer *et al* suggested that under laser annealing at a temperature about 400-500°C, a temperature spike was responsible for the transformation of insulating to conducting for DLC films[6].

Several papers have shown that ion implantation is an useful method for exploring DLC films[2,3,7]. But these papers mainly discussed the changes of resistivity with ion doses. In present paper, Ar ion implantation was used to characterize some properties of DLC films. Ion implantation also provides the possibility of a direct-write mode of producing conducting pathways in these very resistant, hard, insulating layers.

Finally, the different effects of ion implantation, laser and thermal treatments on diamond-like films are discussed.

2 EXPERIMENTAL RESULTS

The DLC films were prepared by R.F. Plasma CVD with (CH_4+ H_2) mixed gas. The samples are divided into two groups. For group A, the power of R.F.discharge is 100W and the temperature of the glass substrate is 250°C, the thickness of the films is about 0.3 micron. For group B, the power is from 40W to 280W and thicknesses are from 0.18 to 1.32 micron, the temperature of the glass substrate is 200°C.

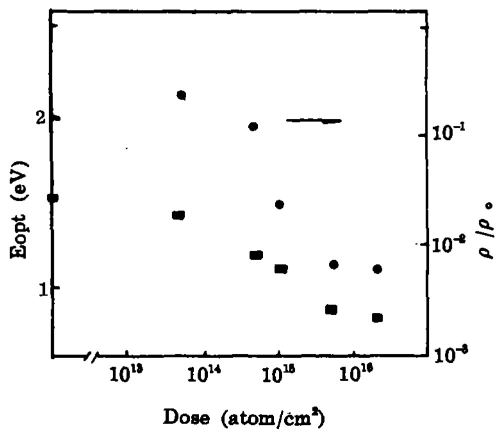


Fig.1 Dependence of resistivities (●) and optical gap (■) on ion doses

Argon ion implantation was completed on the ULVAC IM-200M Machine. For group A, the ion doses were varied from 5×10^{13} cm^{-2} to 2×10^{16} cm^{-2} and

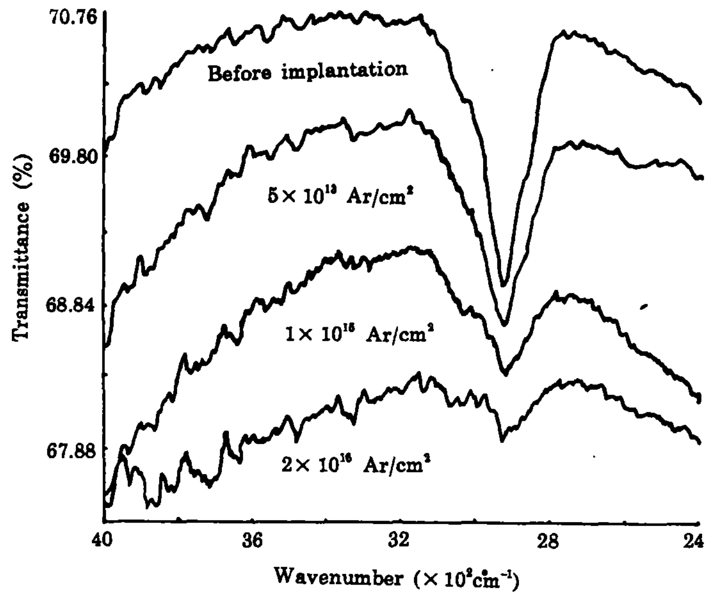


Fig.2 IR spectra of DLC films before and after implantation

ion energy was 140 keV. During implantation, the films were cooled to a temperature below 40°C. The resistances of as-deposited and implanted films were measured with a high resistance meter. Fig.1 shows resistivities changing with ion doses, ρ_0 represents the resistivity of as-deposited films and ρ that of implanted films. The films of group B were implanted with 110 keV Argon ion at a dose of 5×10^{14} cm^{-2} and 2×10^{16} cm^{-2}. It is found that the resistivities decrease 7 orders from the as-deposited value of 10^9 ohm-cm at a dose of 2×10^{16} cm^{-2}, but it does not change at a dose of 5×10^{14} cm^{-2}.

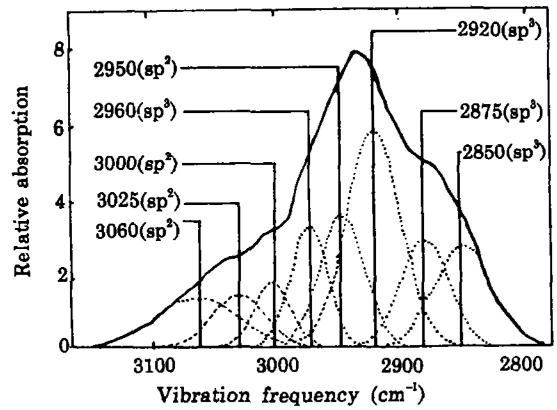


Fig.3 Analysis of infrared absorption spectrum

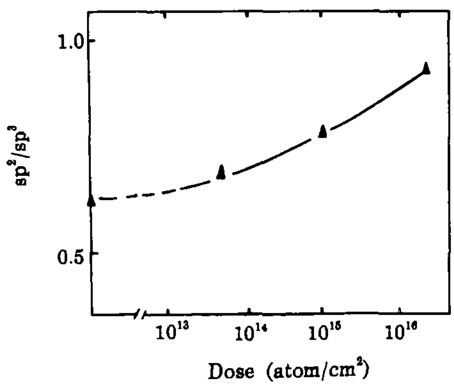


Fig.4 sp^2/sp^3 vs ion doses

The following measurements are only for group A. IR spectra were measured and shown in Fig.2. It is found that the as-deposited films contain diamond-like (sp^3), graphite-like (sp^2) and polymeric components. After implantation both the sp^2 and sp^3 components decreased. In order to obtain the ratio of sp^2 to sp^3, IR spectra of sp^2 and sp^3 components were analyzed. In Fig.3, the spectrum was resolved into eight components[8], which belong to sp^2 or sp^3 bond structure. And from the area of each component, we can obtain the ratio of sp^2 to sp^3. The curve of sp^2/sp^3 versus ion doses is shown in Fig.4.

The values of the optical gap E_{opt} can be obtained by measuring the frequency dependence of optical absorption[9]. A linear relation between $(ah\upsilon)^{0.5}$ and $h\upsilon$ reveals the absorption of electromagnetic radiation by means of direct transition from the tail of density of the states close to the valence band into the corresponding states of the conductivity band. The linear relation which is observed for many amorphous semiconductors can be described by a formula:

$$(ah\upsilon)^{0.5} = B\,(h\upsilon - E_{opt})$$

where $h\upsilon$ is the photon energy, a the absorption coefficient, and B a constant. And then the optical gap E_{opt} can be obtained from the lines in Fig.5. The values of E_{opt} determined are changed from 1.46 eV to 0.83 eV with increasing ion doses and is shown in Fig.1

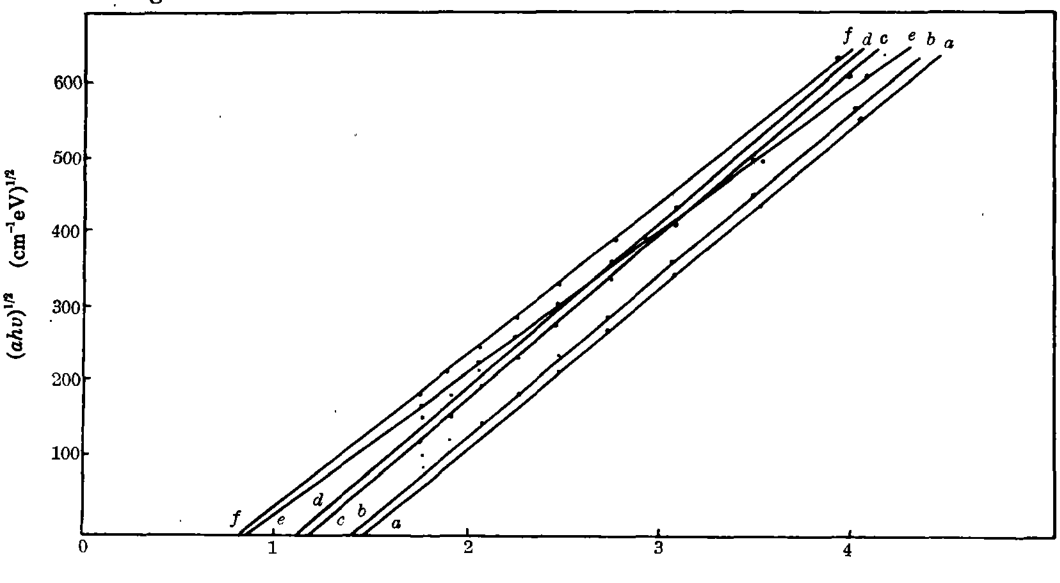


Fig.5 Linear relation of $(ahv)^{0.5}$ vs hv with various doses

(*a*) Before implantation (*b*) 5×10^{13} Ar/cm^2 (*c*) 5×10^{14} Ar/cm^2
(*d*) 1×10^{15} Ar/cm^2 (*e*) 5×10^{15} Ar/cm^2 (*f*) 2×10^{16} Ar/cm^2

Hydrogen contents in DLC films were measured by using the nuclear resonant reaction $^1H(^{19}F, \alpha\gamma)^{16}O$ at resonant energy 6.42 MeV. The total dose of ^{19}F ions is about $10^{13}F/cm^2$. So we can neglect the hydrogen mobility under the bombardment of ^{19}F ion beam. In measurements, $(CH_2)_n$ foil has been used as standards, so we can obtain absolute hydrogen contents. Fig.6 shows a plot of hydrogen contents changed with ion doses at the depths of 50 nm and 150 nm in the films. The depth of 150 nm is the projected range of 140 keV Ar in the film.

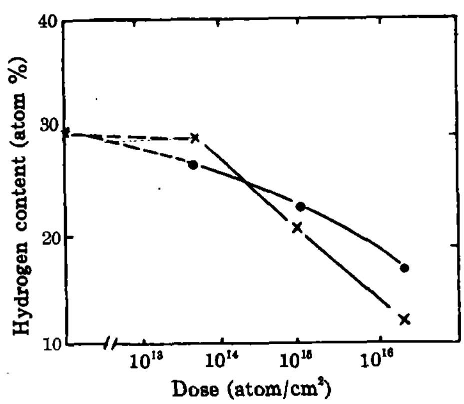


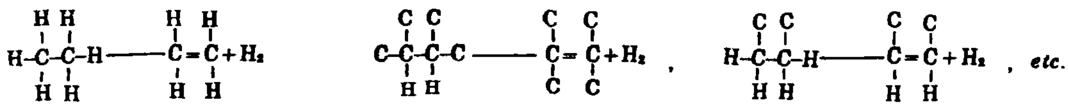
Fig.6 Hydrogen contents at the depth of 50 nm (×) and 150 nm(●) in DLC films vs doses

3 CONCLUSIONS

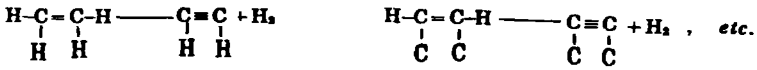
The absolute H contents in films at different depths were carefully determined using nuclear resonant reaction. We consider that all above results are associated with the hydrogen release from the C–H bonds of the films during ion implantation.

While the loss of hydrogen resulted in the increase of dangling bonds of carbon and the increase of amorphous carbon in the DLC films, and then it makes decreases of E_{opt} and resistivities of the films. During the collisions between implanted ions and atoms, the hydrogen release can be explained by considering that some covalent C–H structure is destroyed, loosely–bonded and free stated hydrogen is removed[10]. The loss of C–H bonded hydrogen can be described as follows:

(1) Hydrogen is lost through the transformation of a sp^3 group into a sp^2 group:



(2) A sp^2 group is transformed into a sp^1 group:



In our experiments, IR spectra provide the evidence that both the diamond–like (sp^3) and graphite–like (sp^2) components decrease. However, the Refs.[5,6] showed that the graphite–like (sp^2) component grows and the diamond–like (sp^3) component decreases with laser annealing and thermal annealing, it is due to the temperature spike during the processes. Under ion implantation, there are collisions between ions and atoms, and they result in destruction of C–H bonds and release of hydrogen.

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