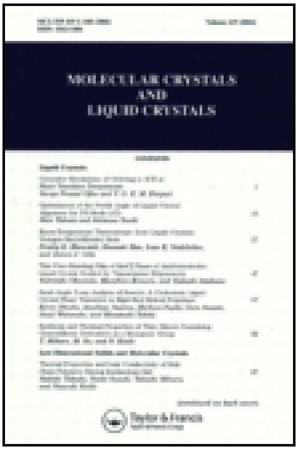

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Fabrication and Characterization of Modified Layer in Ion Implanted Organic Films

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FABRICATION AND CHARACTERIZATION OF MODIFIED LAYER IN ION IMPLANTED ORGANIC FILMS

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Abstract Optical and electrical changes in several kinds of organic films after ion implantation were investigated. Vacuum evaporated organic films were irradiated by 30–100 keV N^+ ion beam. The ion dose was varied from 10^{14} to 10^{16} ions/cm^2. The surface resistivity varies 9 orders of magnitude from the order of 10^{17} ohm/□ to 10^8 ohm/□. Furthermore, the film color changes to dark brown with increasing dose, and main optical absorption peaks of the organic molecule itself decreased. The electrical and optical changes by ion implantation seem to reflect chemical elements and physical properties of these films originated from the molecular structure. Furthermore, the large increase in conductivity by ion beam irradiation is due to the formation of carbon clusters in the organic films. These experimental results suggest that the modification of optoelectric properties and three dimensional wiring in organic films by ion implantation are promising techniques for molecular electronic devices.

Introduction

Electrical and optical properties of organic polymers and molecular films can be modified by relatively low ion fluence. For example, the electrical conductivity of organic films increases several orders of magnitude after Ar^+ or N_2^+ implantation[1-6]. It is believed that the increase of conductivity by the ion beam irradiation is due to the formation of carbonized layer in the organic films. Several authors reported on the conductivity changes of 2 MeV argon ion implanted NiPc and PTCDA films[5].

In this paper, we describe the variations of electrical and optical properties of organic films before and after nitrogen ion (N^+) implantation[7,8]. We have chosen several kinds of organic molecules and polymers, and used low ion accelerating energy(30–100keV) to investigate the relationship between the chemical structure of organic films and the basic parameters of ion implantation, such as ion energy and dose.

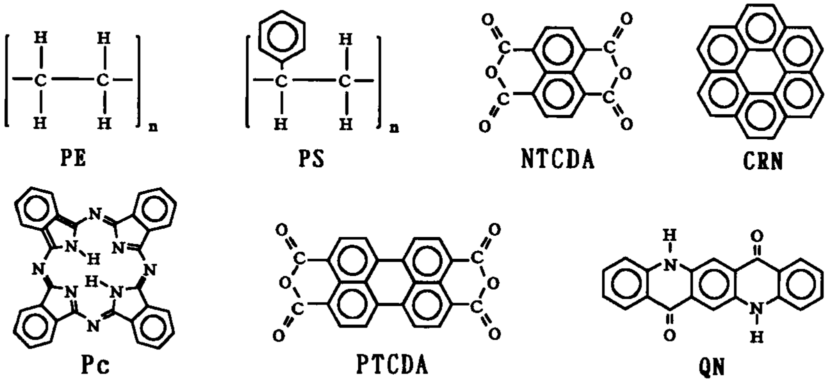


Fig.1 Chemical structures of organic materials.

Experimental

Organic materials used in this study were polyethylene(PE) and polystyrene(PS) as polymers, 3,4,9,10–perylenetetracarboxylic dianhydride(PTCDA), 1,4,5,8–naphthalenetetracarboxylic dianhydride(NTCDA), phthalocyanine(Pc), coronene(CRN), quinacridone(QN). The chemical structure formulas of these materials are shown in Fig. 1.

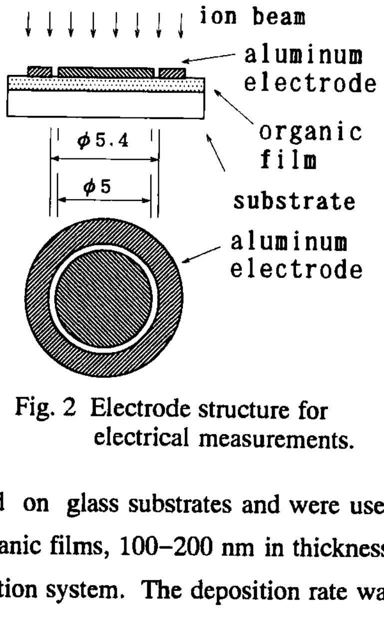


Fig. 2 Electrode structure for electrical measurements.

Organic thin films were vacuum evaporated on glass substrates and were used for the electrical and optical measurements. Organic films, 100–200 nm in thickness, were prepared by a conventional vacuum evaporation system. The deposition rate was maintained at about 10 nm/min. N^+ implantation was performed at an energy range of among 30–100 keV. The ion dose range was varied from 10^{14} to 10^{16} ions/cm^2.

The surface resistivity was measured in the samples with ring type electrodes as shown in Fig. 2. This electrical measurement was performed just after the implantation at each dose without breaking the vacuum. Because, electrical properties of organic films are strongly influenced by atmosphere such as oxygen or other gases. Current–voltage characteristics were measured by applying voltage between –20 and 20 V using a Keithley 617 electrometer.

Optical absorption spectra (λ=300–1100nm) were measured for the N^+ implanted organic films on the glass substrates.

Results and Discussion

Fig.3 shows surface resistivities of N^+ implanted QN films measured at room temperature. The thickness of QN films was about 130 nm. The N^+ accelerating energies were 30, 50, 100keV and the dose range was varied from 10^{14} to 10^{16} ions/cm^2. The surface resistivity of the QN film decreased 7 orders of magnitude after the N^+ implantation. However, the decrease with N^+ dose saturates at the dose range more than 5×10^{15} ions/cm^2. The effect of N^+ accelerating energy on the surface resistivity is clearly seen in Fig.3. As the energy increases, the resistivity decreases. These results can be explained qualitatively by the difference of projected range of N^+ in the films.

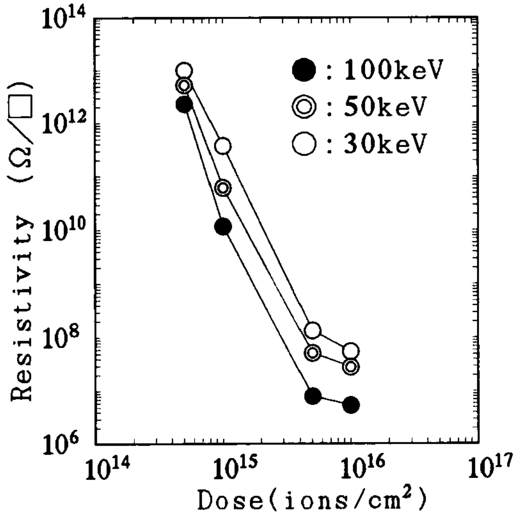


Fig. 3 Surface resistivity changes of QN films by N^+ implantation.

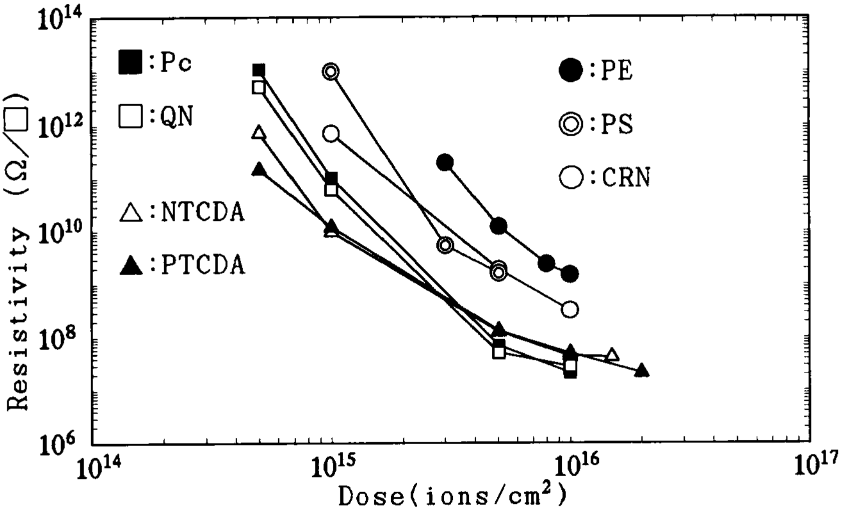


Fig.4 Surface resistivity of various organic films as a function of N^+ dose at 50keV.

	C	H	O	N	benz	mass	m.p.°C	group
QN	20	12	2	2	3	312	*>300	1
Pc	32	18	0	8	4	514	*>300	1
NTCDA	14	4	6	0	2	268	>270	2
PTCDA	24	8	6	0	4	392	>300	2
CRN	24	0	0	0	6	300	440	3
PS	8n	0	0	0	1	104n	230	3
PE	2n	0	0	0	0	28n	>108	3

m.p.:melting point
*:sublimation temperature

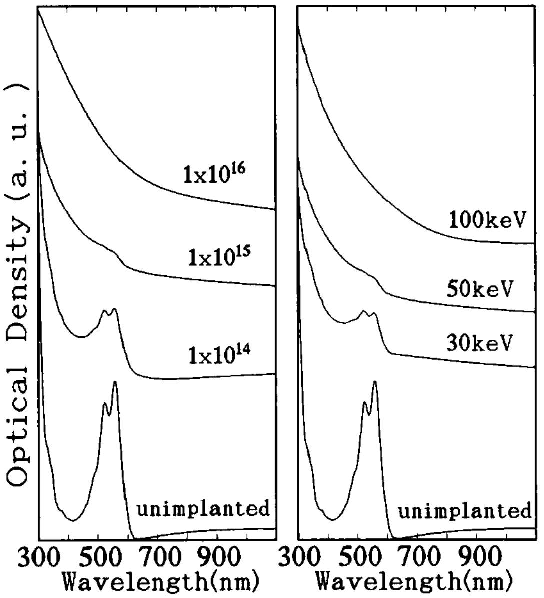
n:number of chain for polymer

benz:number of benzene ring

TABLE 1 The number of chemical elements and thermally property of organic materials.

A significant decrease of the electrical resistivity is also observed for other films used here. However, the variation of the electrical resistivity for ion energy and ion dose depend on the organic materials.

Fig.4 shows the surface resistivity of all the samples as a function of N^+ dose. The N^+ accelerating energy was 50 keV and the dose range was varied from 10^{14} to 10^{16} ions/cm^2. These results indicate that the behavior of resistivity for implanted films is classified into 3 groups. First group (1) is QN and Pc, second one (2) is NTCDA and PTCDA, third one (3) is CRN, PS and PE. Table 1 shows the number of chemical elements, benzene rings, mass and physical property (melting point or sublimation temperature) of organic materials. The first group which contains



(a) 50keV (b) 1x10^{15}(ions/cm^2)

Fig. 5 Optical absorption spectra of QN films after and before implantation.

nitrogen atoms show a large change in resistivity and a sudden saturation at the dose of 5x10^{15} N^+/cm^2. The resistivities of the second group which contains oxygen atoms show a slightly slow change. This result may be due to the similarity between the chemical structures of PTCDA and NTCDA as shown in Fig.1. The resistivities of the third group which has only carbon and hydrogen atoms remain high resistivities compared with other two groups. The variation of the surface resistivities by N^+ implantation strongly depends on the chemical structure, especially their chemical elements such as N and O atoms. However, the thermal properties such as melting point or sublimation temperature seem to be independent of the conductivity changes by ion implantation.

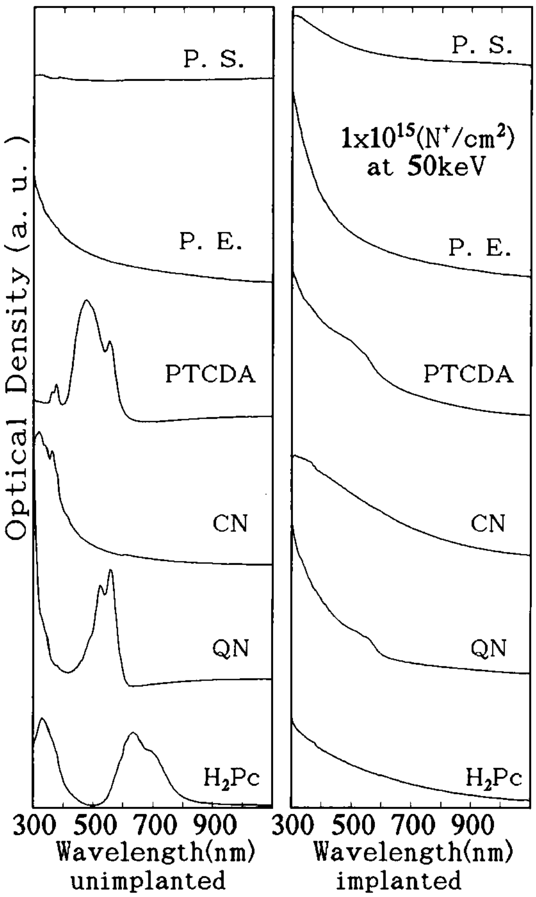


Fig. 6 Optical absorption spectra of all the samples after and before implantation.

The colors of unimplanted PTCDA, NTCDA, CRN, Pc, QN, PE and PS films are dark red, yellow, yellow, blue, dark purple, transparent and transparent, respectively. The color of implanted films turns into a deep brown with increasing dose in all the samples. Optical absorption spectra of QN films before and after N^+ implantation at 30–100 keV are shown in Fig.5. The ion dose range was changed from 10^{14} to 10^{16} ions/cm^2. The main absorption peaks of QN film decreased gradually with increasing dose, and the absorption spectrum of the film was changed to broad and monotonical one.

A similar change of the absorption spectra is also observed in other samples. Fig.6 shows the optical absorption spectra for all the samples used here after and before implantation. In this case, the accelerating energy and dose were 50keV and 1×10^{15} ions/cm^2, respectively. These results indicate that carbon clusters are created in the organic film by N$^+$ implantation.

Conclusion

We have investigated the electrical and optical properties of several kinds of organic films after N$^+$ implantation. The surface resistivities of N$^+$ implanted organic films were decreased by several orders of magnitude with respect to those of unimplanted ones. The color of implanted films turns into a deep brown and the absorption spectra lose their own shape with increasing dose. It is suggested that electrically conductive carbon-cluster-layer is created in the organic films by N$^+$ implantation. These results obtained here demonstrate that the ion implantation into organic films is one of the key technologies for the fabrication of molecular electronic devices, since this technique has a possibility to make modified layers and three dimensional wires between molecular devices.

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