

The study of damaged layer induced by Ar⁺ irradiation in plasma-polymerized thiophene film

Zhi Shen Tong^a, Tian Shu Pu^a, Mei Zhen Wu^a, Zheng Yang Zhang^a, Jing Zhang^a,
Ruo Peng Jin^a, De Zhang Zhu^b, De Xin Cao^b, Fu Ying Zhu^b, Jian Qing Cao^b

^a Department of Basic Sciences, China Textile University, Shanghai 200051, China

^b Shanghai Institute of Nuclear Research, Chinese Academy of Science, Shanghai 201800, China

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Abstract

A dense organic film was prepared by plasma polymerization from thiophene. 100 keV Ar⁺ irradiation at a fluence of 5×10^{15} ions cm⁻² was used to produce a conducting layer due to damage. The characteristics of the damaged layer have been explored on the basis of studies on the optical properties and carrier transport.

Keywords: Plasma polymerization; Thiophene; Damaged layer; Hydrogenated amorphous carbon; Irradiation; Films

1. Introduction

It is well known that a steady conducting layer beneath the surface of polymers has been induced by energetic ion (keV–MeV) irradiation. The characteristics of the bombarded layer should be modified with the deposited energy density. At low energy density (10^{22} – 10^{24} eV cm⁻³), the interaction between energetic ions and polymer results in chain scission, production of new bonds (such as double bonds and crosslinking) and molecular emission. On increasing the energy density to 10^{24} – 10^{26} eV cm⁻³, the damaged layer continues to evolve, showing spectroscopic characteristics close to those of hydrogenated amorphous carbon film (a-C:H) [1].

Polythiophene film and other conducting polymers with conjugated double bonds have attracted much attention over the last decade. Doped polythiophene prepared by electrochemical polymerization is known to reveal an electrical conductivity between 10^{-2} and $10^2 \Omega^{-1} \text{cm}^{-1}$ which depends on its structure and hence on the conditions of synthesis. The recent work of Tanaka et al. [2] on plasma-polymerized thiophene film showed that the thiophene rings are largely destroyed, but the electrical conductivity of the sample after exposure to iodine vapour still increases by four to six orders of magnitude. Recently, we have also reported the preparation of an organic film by plasma polymerization of thiophene and investigated its composition and structural characteristics as well as the doping effect of 24 keV I⁺ ion implantation [3].

In the present article, we have explored the transport process of charge carriers in the temperature range 240–280 K for the bombarded layer of plasma-polymerized thiophene film irradiated with 100 keV Ar⁺ at a fluence of 5×10^{15} ions cm⁻². Moreover, we have calculated the complex refractive index, $N_1 = n_1 + ik_1$ for the bombarded layer by analyses of reflectance and transmittance data using the transfer matrix method. Then the optical properties of the irradiated layer have been investigated in detail. It should be mentioned that, because the thickness of the irradiated layer was smaller than that of the pristine layer, the calculation of optical constants for this layer was referred to a system consisting of two thin films and one thick plate: irradiated layer *l*/pristine layer *f*/substrate *s*. We think that these results are useful to characterize the ion-bombarded layer further.

2. Experimental

Plasma polymerization was performed in a glass-tube chamber with capacitive coupling at a frequency of 13.56 MHz. The schematic representation of the apparatus used for r.f. plasma polymerization was reported elsewhere [4]. The reaction chamber had been evacuated to a pressure of 0.5 Pa before the monomers were introduced. During the process of plasma polymerization, the total gaseous pressure was adjusted to 9 Pa, and the r.f. power was about 25 W. The rate

of film growth and its density were estimated to be about 6.5 nm min^{-1} and 1.65 g cm^{-3} , respectively.

The measurements of near-IR to UV spectra were carried out for the sample on a glass substrate using a Perkin-Elmer Lambda 9 UV-Vis-NIR spectrophotometer. During the Ar^+ ion bombardment, the incident energy and fluence were maintained at 100 keV and $5 \times 10^{15} \text{ ions cm}^{-2}$, respectively; the ion beam current density was less than $0.2 \mu\text{A cm}^{-2}$ to avoid macroscopic heating of the specimen. The electric resistance of the pristine sample was determined at room temperature by the conventional two-electrode technique. The determinations of electrical resistance in the irradiated layer were performed in the temperature region of 240–280 K with van der Pauw's method. The linear relation between the current and voltage indicated that ohmic contacts were satisfying. The sheet resistance determined in the irradiated layer was converted into bulk resistivity by assuming that the thickness of the conducting layer was equal to the ion-beam penetration depth $R_p + \Delta R_p$, where R_p is the average projective range and ΔR_p is its straggle. According to TRIM-91, R_p and ΔR_p are found to be 118.9 nm and 32.3 nm, respectively, for the specimen irradiated by 100 keV Ar^+ ions.

3. Calculation of complex refractive index for the case of the irradiated layer *l*/pristine layer *f*/substrate *s*

The complex-amplitude reflection and transmission coefficients of a pile of films have been recently reported by Harbecke [5] as a product of transfer matrices. We now apply this method to the following situation: a normal plane electromagnetic wave is incident on a system of medium *a*/irradiated layer *l*/pristine layer *f*/substrate *s*/medium *b* (both media *a* and *b* are assumed to be vacuums). Because the substrate is sufficiently thick, light interferes incoherently between its front and back surfaces. Thus, the reflectance and transmittance of this system are given by

$$R_{ab} = |r_{as}|^2 + \frac{|t_{as}t_{sa}\rho_{sb}\phi_s^2|^2}{1 - |r_{sa}\rho_{sb}\phi_s^2|^2} \quad (1)$$

$$T_{ab} = \frac{|t_{as}\phi_s\tau_{sb}|^2}{1 - |r_{sa}\rho_{sb}\phi_s^2|^2} \quad (2)$$

where r_{as} and t_{as} denote complex-amplitude reflection and transmission coefficients, respectively, when the light beam passes through the pile of medium *a*/irradiated layer *l*/pristine layer *f*/substrate *s*.

We successively apply the transfer matrix to this pile, and the following expressions are obtained:

$$r_{as} = \frac{\rho_{al} + \phi_l^2\rho_{lf} + \rho_{fs}(\rho_{al}\rho_{lf}\phi_l^2 + \phi_l^2\phi_f^2)}{1 + \rho_{al}\phi_l^2\rho_{lf} + \rho_{lf}\phi_l^2\rho_{fs} + \rho_{al}\phi_l^2\phi_f^2\rho_{fs}}$$

$$t_{as} = \frac{\tau_{al}\phi_l\tau_{lf}\phi_f\tau_{fs}}{1 + \rho_{al}\phi_l^2\rho_{lf} + \rho_{lf}\phi_l^2\rho_{fs} + \rho_{al}\phi_l^2\phi_f^2\rho_{fs}}$$

where ρ and τ are Fresnel's complex amplitude reflection and transmission coefficients, respectively. $\phi_l = \exp(i\omega N_l d_l/c)$, where N_l is the complex refractive index ($N_l = n_l + ik_l$) of the irradiated layer and d_l is its thickness. r_{sa} and t_{sa} in Eqs. (1) and (2) are the corresponding coefficients, respectively, with the opposite direction of light through the pile. We may give the expressions for them by the same approach. The complex refractive indices N_l for pristine sample and N_s for substrate have been obtained by us [3]. So, from Eqs. (1) and (2), we can obtain the refractive index n_l and extinction coefficient k_l for the irradiated layer. Furthermore, the complex dielectric function of the irradiated layer $\epsilon_l = \epsilon_1 + i\epsilon_2$ can be also calculated according to $\epsilon_1 = n_l^2 - k_l^2$ and $\epsilon_2 = 2n_l k_l$. The real and imaginary parts of the complex dielectric function may be transformed using the Kramers–Kronig relations.

4. Results and discussion

4.1. FT-IR analysis

Fig. 1 shows the FT-IR spectrum for the damaged layer induced by 100 keV, $5 \times 10^{15} \text{ Ar}^+$ ions cm^{-2} irradiation in plasma-polymerized thiophene film. As a comparison the

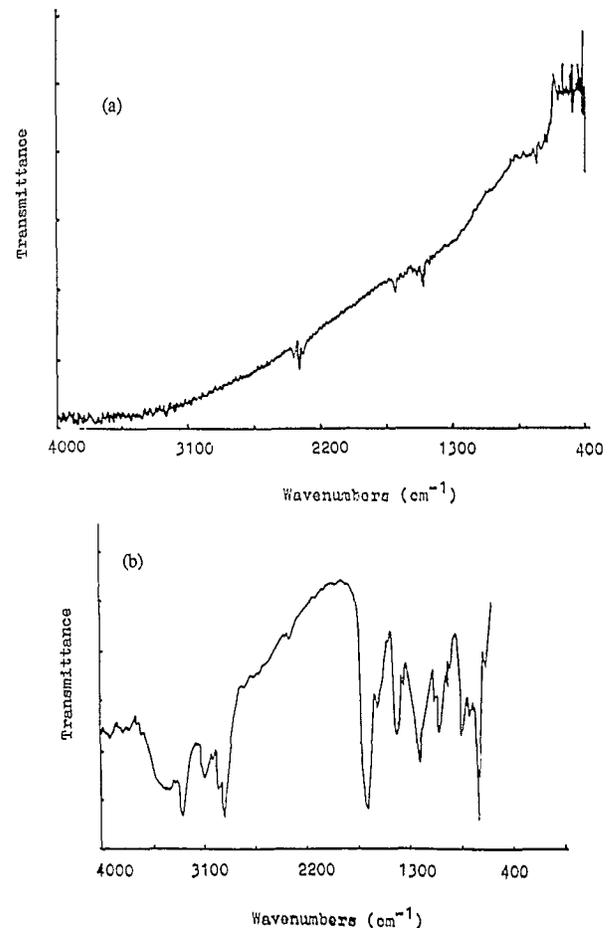


Fig. 1. FT-IR spectra for the 100 keV, $5 \times 10^{15} \text{ Ar}^+$ ions cm^{-2} irradiated sample (a) and the pristine film (b). The spectrum of the pristine film is quoted from [3].

spectrum of the pristine film is quoted, also shown in this figure, from our previous work [3]. In order to examine the IR spectral characteristics for the irradiated layer, the thickness of the sample used in Fig. 1(a) was less than 200 nm, which approximates to the penetration of 100 keV Ar⁺. The measured result shown in Fig. 1(a) indicates that absorbance almost monotonically increases with the wavenumber; this is the characteristic of materials containing charge carriers [6]. However, some kinds of vibration modes are still visible in Fig. 1(a). The absorption at 760 cm⁻¹ arises from out-of-plane C–H bending on the aromatic ring [7], 1575 cm⁻¹ is due to C=C stretch of sp² [8]. The absorption between 2200 and 2560 cm⁻¹ can be assigned to –C≡N or –N=C=O [4], while the feature at 1705 cm⁻¹ is obviously attributed to the carbonyl [8]. The presence of small amounts of nitrogen and oxygen is probably caused by air contamination on the sample surface. We should note that the C–H stretch absorption in the 3000 cm⁻¹ region does not appear in this figure; it may result from the mergence by the electronic carrier absorption and from the small thickness of the irradiated layer.

4.2. Optical constants

Because of the monotonical increase of the electronic carrier absorbance at the wavenumbers above 1600 cm⁻¹, resulting in the mergence of some vibration absorption concerned with carbonic radicals, we cannot understand the microstructure in detail from FT-IR measurement. However, the optical constants are useful to explore the microstructure of materials. The imaginary part ϵ_2 of the complex dielectric function is particularly important because it can be related to electronic transitions. A sum rule involving ϵ_2 has been used to investigate the electronic configuration for carbonaceous materials by some authors. In this subsection, we show the results of optical constants for the plasma-polymerized thiophene film irradiated with 100 keV, 5×10^{15} Ar⁺ ions cm⁻² by the method mentioned in Section 3. In the following subsection, we calculated the ratio of sp² carbon to sp³ carbon using the sum rule.

Refractive index n_1 and extinction coefficient k_1 for the bombarded layer of plasma-polymerized thiophene irradiated by 100 keV, 5×10^{15} ions cm⁻² Ar⁺ are shown in Fig. 2. Figs. 3 and 4 report the real part ϵ_1 and imaginary part ϵ_2 of the complex dielectric function, respectively. For comparison, the complex dielectric function of a-C:H is quoted in Fig. 5 [7]. Results show that the spectroscopic characteristic for the irradiated layer is similar to that of hydrogenated amorphous carbon (a-C:H) after annealing at 400–500 °C. Moreover, according to $\alpha = 4\pi k/\lambda$, the absorption coefficient α_1 for the bombarded layer, as shown in Fig. 6, was also obtained. Figs. 4 and 6 indicate that a small absorption band appears at the photon energy near 0.5 eV. This band has also been observed in the spectrum of a-C:H prepared by r.f. plasma deposition from benzene vapour by Dischler et al. [9]. It is possibly a doping effect due to trace impurity.

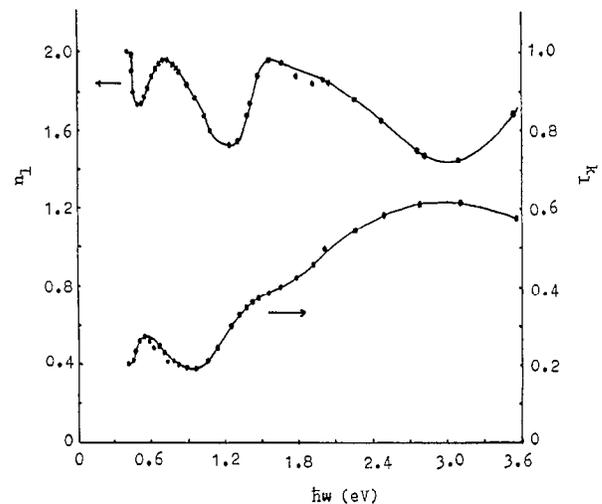


Fig. 2. Refractive index n_1 and extinction coefficient k_1 for the irradiated layer vs. photon energy $\hbar\omega$. Ar⁺ energy and fluence were 100 keV and 5×10^{15} ions cm⁻², respectively. $d_1=0.1512$ μm , $d_f=0.3288$ μm , $d_s=1$ mm.

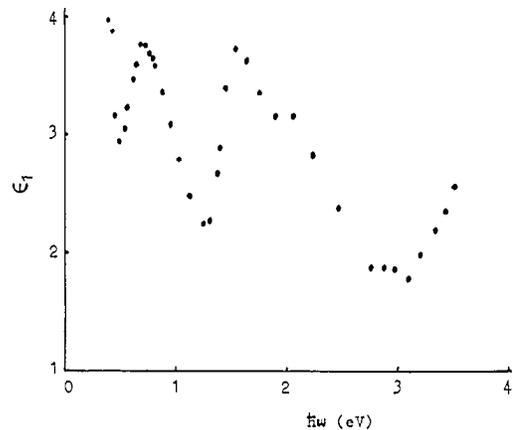


Fig. 3. Real part ϵ_1 of the dielectric function for the irradiated layer vs. photon energy $\hbar\omega$.

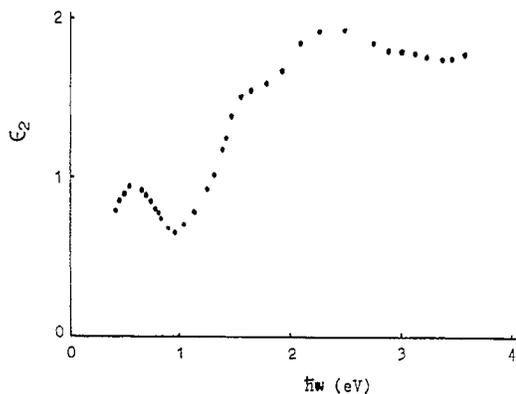


Fig. 4. Imaginary part ϵ_2 of the dielectric function for the irradiated layer vs. photon energy $\hbar\omega$.

Darkening and conducting in the film after irradiation with high energy density are due to the degradation of polymer. From our article on plasma-polymerized pyrrole film [10], the damage of the film induced by Ar⁺ ion bombardment at an energy density of 5×10^{25} eV cm⁻³ results in depletions of hydrogen and nitrogen by about 11.2 and 31.8%, respec-

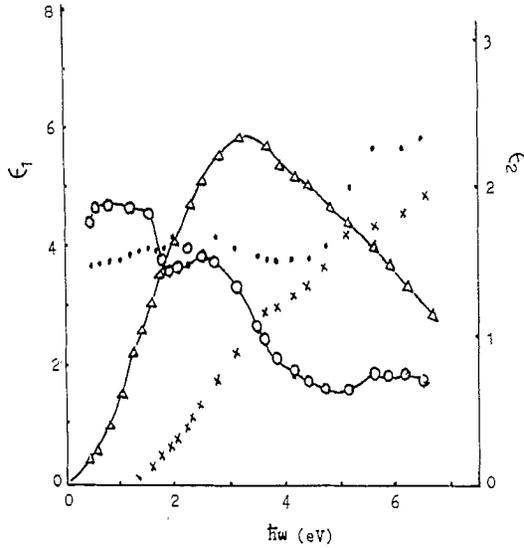


Fig. 5. Complex dielectric function of a-C:H as a function of photon energy: ● and × denote ϵ_1 and ϵ_2 , respectively, for as-prepared film; ○ and △ denote ϵ_1 and ϵ_2 , respectively, after 500 °C heat treatment (quoted from Ref. [7]).

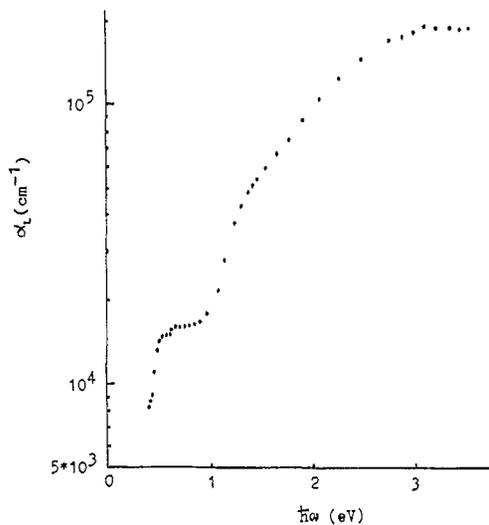


Fig. 6. Absorption coefficient α_1 of irradiated layer vs. photon energy $\hbar\omega$.

tively. For the case of plasma-polymerized thiophene film bombarded with 100 keV Ar^+ at a fluence of 5×10^{15} ions cm^{-2} (corresponding to a deposited energy density of 3.3×10^{25} eV cm^{-3}), it is possible to suppose that the depletion of hydrogen is approximately the same as that of the irradiated plasma-polymerized pyrrole. Hence, we estimated that about 31.6 at.% of hydrogen and a few percent of sulfur are present in the damaged layer of plasma-polymerized thiophene film.

4.3. Application of a sum rule

In order to examine the proportion of sp^2 sites in the damaged layer, a sum rule as shown in following equation has been applied:

$$\int_0^{\infty} \omega \epsilon_2(\omega) d\omega = \frac{1}{2} \pi \omega_p^2 \quad (3a)$$

where ω_p is the free-electron plasma frequency. It is known that Eq. (3a) is completely general and valid for an arbitrary many-electron system [11]. Because of

$$\omega_p^2 = \frac{e^2}{\epsilon_0 m} N n_{\text{eff}}$$

Eq. (3a) reduces to

$$n_{\text{eff}} = 0.767 \frac{A}{\rho} \int_0^{E_M} E \epsilon_2(E) dE \quad (3b)$$

Here n_{eff} is the effective number of valence electrons per atom taking part in the optical transition in the range of photon energies up to E_M , E being the photon energy in eV. A is the atomic mass of the substance in a.m.u.; ρ its density contribution in kg m^{-3} to the total film density. It is generally accepted that in material simultaneously containing π and σ electrons, electronic absorption below 7 eV is almost entirely due to transitions involving electrons in π orbitals; covalent electrons such as the σ electrons of C-C and C-H bonds make no contribution until 9 eV. Thus, the value of A in Eq. (3b) is 12; ρ is the density contribution of carbon which can be estimated from the total density of the irradiated layer and its composition. The thickness of the irradiated layer is less than 200 nm, which is too thin for density determination in our laboratory; hence, the total density of the irradiated layer was approximated to that of pristine film.

Fig. 7 shows the plot of effective number of valence electrons per carbon atom taking part in optical transitions for the irradiated layer as a function of photon energy E_M . As a

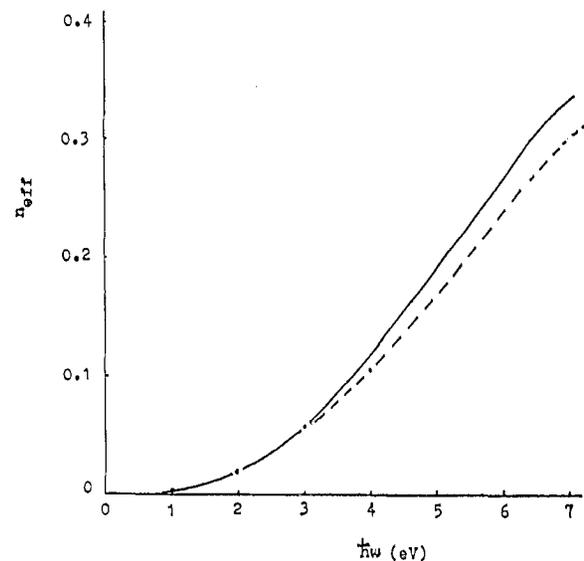


Fig. 7. Plot of the effective number of valence electrons per carbon atom taking part in optical transitions in the range of photon energies up to E_M : ---, data for the 100 keV, 5×10^{15} Ar^+ ions cm^{-2} irradiated layer; —, result for a-C:H after 500 °C annealing reproduced from [7].

comparison, the result of a-C:H film by McKenzie et al. [7] is also shown in this figure. The proportion of sp^2 in the total carbon sites is evaluated by the ratio of n_{eff} for the irradiated layer at 7 eV to that of graphite. A reasonable extrapolation of the experimental data is shown as a dotted line in Fig. 7. The value of n_{eff} at 7 eV for the irradiated layer is approximately equal to 0.3, while the value of that for graphite is 0.85 from Ref. [12]; hence, we obtained the sp^2 proportion to be 35.6%. The same conclusion may be also obtained from another method to estimate the average number of π electrons per carbon atom. From Ref. [7], McKenzie et al. have given the sp^2 proportion for their annealed a-C:H film to be 0.41; by multiplying this value with the ratio of n_{eff} at 4 eV for our irradiated layer to that of the sample of McKenzie et al. (shown as the solid line in Fig. 7), we yield a value of 36% for the sp^2 proportion in the bombarded layer. This result coincides with those of a-C:H obtained by other authors. For example, Dischler et al. [8] have shown that the a-C:H film prepared by r.f. plasma deposition of benzene contains 39 at.% of hydrogen, in which about one-third of the carbon atoms are in the sp^2 electron configuration.

4.4. Optical gap

For amorphous semiconductors if the dipole matrix element for transition is independent of energy and both valence and conduction band edges are approximately parabolic, then the following equation is obtained [12]:

$$\omega^2 \epsilon_2(\omega) = B(\hbar\omega - E_g)^2 \quad (4)$$

which defines the optical gap E_g . It is necessary to note that Eq. (4) may not definitively imply the existence of the true energy gap. The tails of localized states usually occur above the valence band mobility edge and below the conduction band mobility edge. So the gap of amorphous semiconductors should strictly be referred to as pseudo gap or mobility gap.

Fig. 8 indicates the linear dependence of $\hbar\omega\epsilon_2^{1/2}$ on photon energy for the damaged layer. The optical gap E_g is deter-

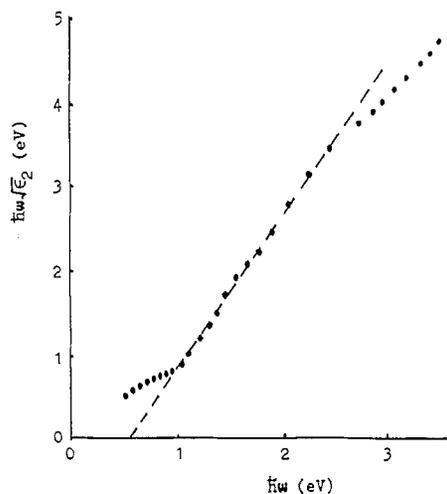


Fig. 8. Plot of $\hbar\omega\epsilon_2^{1/2}$ vs. photon energy $\hbar\omega$ for the damaged layer of plasma-polymerized thiophene film irradiated by 100 keV Ar^+ at the fluence of 5×10^{15} ions cm^{-2} .

mined to be 0.55 eV by extrapolating the linear plot to the energy axis, which is approximately the same as that of a-C:H heated at 500 °C for 100 h [7]. Deviations of the data from linearity at low energies arise from transitions in exponential band tails below the mobility edge and are characteristic of amorphous semiconductors. In the high-energy region, a drop of data from linearity has also been observed for a-C:H film heated at 500 °C by McKenzie et al. [7].

Robertson et al. [13,14] have recently proposed a model for a-C:H. According to this model, in addition to fourfold sp^3 sites, a-C:H still contains a considerable proportion of threefold coordinate sp^2 sites. The most stable arrangement of sp^2 sites is in compact clusters of fused sixfold rings (graphitic layer). These graphitic clusters, a typical structure of planar aromatic rings, are interconnected by randomly oriented tetrahedral sp^3 bonds. The hydrogen may be bonded to carbon sp^3 or sp^2 sites. The nature of the disorder in a-C:H is to allow a gap to open up. The optical gap E_g depends on the medium range order and varies inversely with the sp^2 cluster size. For the compact cluster of fused sixfold rings E_g is given by the following equation:

$$E_g = \frac{2|\beta|}{M^{1/2}} \quad (5a)$$

where β is the interaction between two nearest neighbour π orbitals; M is the number of benzoid rings inside the cluster. If we propose $\beta = -2.9$ eV, then we have [1,13]

$$E_g = 6/M^{1/2} \quad (5b)$$

According to the theory of Robertson et al., the optical absorption edge, as shown in Fig. 6, may provide some of the most valuable data on the microstructure of the damaged surface layer. The sum rule can be used to evaluate the fraction of the sp^2 configuration, as we have done in the above subsection, while the optical absorption edge gives information on the degree of clustering of the sp^2 sites. Fig. 6 shows a broad slope of the optical absorption edge; this characteristic is the general feature for both a-C and a-C:H. From the model of Robertson et al., the broad slope of absorption edge is due to the wide range of cluster sizes. It means that a-C and a-C:H as well as our damaged surface layer contain a series of π -bonded clusters of varying size and consequently of varying gap width. The Tauc plot, a linear dependence of $\hbar\omega\epsilon_2^{1/2}$ on the photon energy, as shown in Fig. 8, has given the minimum gap of 0.55 eV; using Eq. (5b) the number of benzoid rings M inside the largest cluster is equal to 119, corresponding to the largest cluster dimension 2 nm in the damaged layer.

4.5. D.c. electrical resistivity

The d.c. resistivity of pristine film at room temperature is of the order of 10^{13} Ω cm, while the resistivity at 283 K in the damaged layer of plasma-polymerized thiophene irradiated with 100 keV Ar^+ at a fluence of 5×10^{15} ions cm^{-2} is

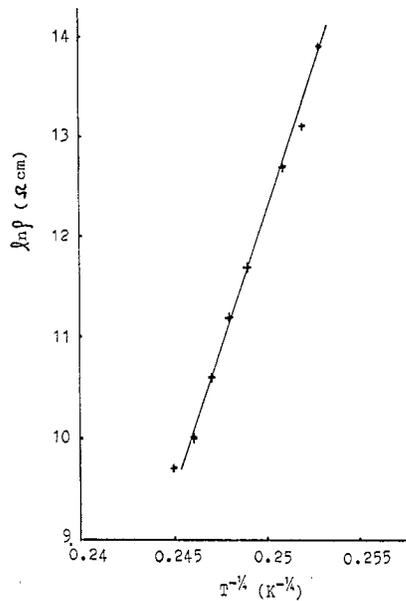


Fig. 9. D.c. resistivity in the bombarded layer of plasma-polymerized thiophene film irradiated with 100 keV, 5×10^{15} Ar⁺ ions cm⁻² as a function of temperature in the region 240–280 K.

equal to $1.5 \times 10^4 \Omega \text{ cm}$. The variation of d.c. resistivity with temperature in the range of 240–280 K can be analysed approximately in terms of the 3D variable range hopping (VRH) mechanism (the region of temperature is small due to the experimental difficulty). McKenzie et al. have obtained the same conclusion on the temperature dependence of electrical conductivity over the temperature range 77 to 500 K for a-C:H film after annealing at 773 K [7].

From VRH theory [15]

$$\rho = \rho_0 \exp(T_0/T)^{1/4} \quad (6)$$

The most possible hopping distance of the charge carriers is given by

$$R = \left[\frac{3}{2\alpha(4\pi/3)N(E_F)k_B T} \right]^{1/4} \quad (7)$$

where $T_0 = 16\alpha^3/k_B N(E_F)$, α is the coefficient of the exponential decay of the localized wavefunction, and then α^{-1} is equivalent to the radius of localized state. $N(E_F)$ is the density of states at the Fermi level. If $\alpha^{-1} = 0.5 \text{ nm}$, from Fig. 9 we obtain $N(E_F) = 2.4 \times 10^{16} \text{ eV}^{-1} \text{ cm}^{-3}$ and $R = 24 \text{ nm}$. This value of $N(E_F)$ is two orders of magnitude lower than that of a-C:H film after annealing at 500 °C [7].

However, some authors have indicated that the property of a-C:H depends sensitively on the microstructure and, thus, on the method and parameters of deposition. The defect states in both a-C and a-C:H films always present a continuous distribution across the pseudo gap and control the transport property allowing conduction by VRH. Experimentally, these defect states can be determined from the hyperfine ESR spectrum. In general, spin densities in the range 10^{16} – 10^{18} cm^{-3} are found which also vary over two orders of magnitude [14]. The reason for smaller $N(E_F)$ found in our irradiated sample is probably because severe disorders presented in the bom-

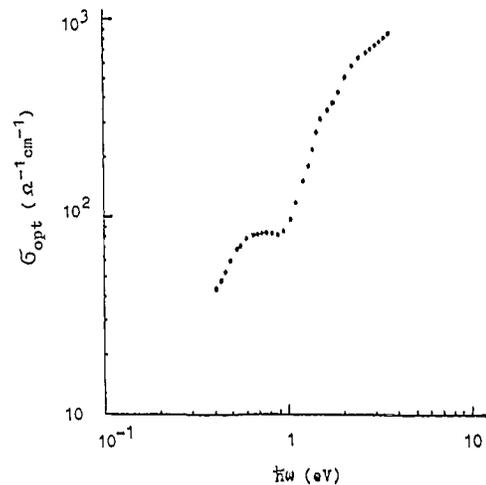


Fig. 10. Optical conductivity in the irradiated layer vs. photon energy.

barded layer induce part of the defect states to localize tightly. It seems that these tightly localized π electrons cannot participate in the transport process in the experimental temperature range; hence, the density of states at the Fermi level obtained from the measurement of electrical resistivity is drastically reduced.

The work of Savvides [12] has shown that for the deposited amorphous carbon film about half the π electrons involved in interband transitions are tightly bound and do not contribute to polarization. Recently, Lee et al. [16], from the investigation of reflectance spectra of polyaniline, also indicated that, for the sample of emeraldine base protonated with sulfuric acid (PANI-H₂SO₄), the states near the Fermi energy are localized. This localization arises from the severe disorder present in PANI-H₂SO₄ (Anderson localization).

4.6. Optical conductivity

It is known that the electrical conductivity is determined by the product of charge carrier concentration and its mobility. For the case of d.c. conduction, the disorders, both short and long ranges, control the transport process. In contrast, the optical conductivity σ_{opt} associated with electronic polarization and transition is mainly related to electronic states and charge carrier concentration. Thus, according to $\sigma_{\text{opt}} = \omega\epsilon_0\epsilon_2$, we calculated σ_{opt} for the irradiated layer of plasma-polymerized thiophene film [17]. Fig. 10 shows that σ_{opt} is in general larger than d.c. conductivity by several orders of magnitude. The discontinuous increases of the optical conductivity for the photon energies below 1 eV are possibly induced by the doping effect.

5. Conclusions

A dense organic film was obtained by plasma polymerization of thiophene. From the near-IR to UV reflectance and

transmittance data of the film irradiated with 100 keV, 5×10^{15} Ar⁺ ions cm⁻², the optical properties have been investigated by using the transfer matrix method. Results show that for the deposited energy density of 3.3×10^{25} eV cm⁻³, the irradiated layer is equivalent to an a-C:H film subjected inhomogeneously to annealing due to the microscopic heating. In this irradiated layer, about 36% of carbon atoms are in the sp² configuration. The optical gap E_g is 0.55 eV. The number of rings inside the largest graphitic cluster is estimated to be 119, corresponding to a cluster dimension of 2 nm. The variation of d.c. resistivity with temperature in the range of 240–280 K can be analysed in terms of the 3D VRH method. Because of the disordering, d.c. conductivity is generally several orders of magnitude lower than optical conductivity.

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