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Temperature dependence of the optical-absorption edge in C_{60} thin films

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The optical absorption edge of semiconductor C_{60} films is studied in a wide temperature range of 8.8–470 K. We find three temperature regimes for both the optical gap E_o and the Urbach tail parameter E_u: in the range $T<150$ K, they do not change; $150<T<260$ K, they change gradually; and $T>260$ K, they change rapidly. We also find that the subgap absorption increases with prolonged exposure of the film to air but the Urbach tail parameter E_u is not affected. The results are discussed in terms of the relation of the electron density of states to the molecular orientational disorder and the structural phase transition. [S0163-1829(98)05939-6]

I. INTRODUCTION

The electronic densities of states of solid C_{60} and C_{70} fullerenes exhibit narrow electronic energy bands close to those of the isolated molecules.[1] It has been found that the energy of the fundamental allowed transition between the highest occupied molecular orbital and the lowest unoccupied molecular orbital in solid C_{60} is ≈ 2.3 eV,[2] while the optical-absorption edge extends to a much lower energy with an exponential tail. The optical gap is found to be ≈ 1.6 eV in C_{60} films at room temperature.[3,4] Several possibilities have been suggested to explain the absorption edge, such as (a) the presence of a weakly allowed transition level in the C_{60} molecule,[5] and (b) C_{60} intercalation with impurities.[3] Additionally, because the C_{60} molecule is not perfectly spherical, there are two inequivalent orientations related by a $\pi/3$ rotation about a threefold axis.[6–10] The orientational order/disorder of C_{60} molecules plays an important role in determining the physical properties of the materials. It has been found theoretically that the density of the electronic states for the fully ordered system has sharp peaks, whereas for the disordered system it has a rather smooth band with band tails.[7] There are three temperature regimes of the orientational disorder:[6–10] (1) $T<150$ K, orientation frozen phase, the two low-energy orientations are found to freeze out in a 5:1 ratio; (2) $150<T<260$ K, orientational disorder phase; and (3) $T>260$ K, free rotation phase. A first-order structural transition from face-centered-cubic (fcc) to simple-cubic phases was observed at 260 K. How does the molecular orientation affect the optical absorption edge? It needs to be studied both experimentally and theoretically.

Generally, the tail of the optical-absorption edge of a semiconductor exhibits the characteristic Urbach form

$$\alpha(E)=\alpha_0 \exp(E-E_1)/E_u, \tag{1}$$

where α_0 and E_1 are constant. Based on studies of noncrystalline semiconductors, the optical gap E_o can be deduced from the optical-absorption edge near the intrinsic transition by use of the Tauc model,[11]

$$\alpha(E)h\nu \propto (E-E_o)^2, \tag{2}$$

which is based on the assumption of a constant optical-matrix element and a parabolic density of states. Furthermore, both thermal- and structure-disorder parameters can be deduced from the Urbach tail parameter E_u.[11] The definition of site disorder as the mean-square dispersion of a generalized coordinate, $X=\langle q^2\rangle_x/\langle q^2\rangle_0$, suggests the following general form for the Urbach tail parameter E_u:

$$E_u(T,X)=\left(\frac{\theta_E}{\sigma}\right)\left\{\frac{1}{\exp(\theta_E/T)-1}+\frac{1+X}{2}\right\}, \tag{3}$$

where $\theta_E \approx \frac{3}{4}\theta_D$ is the Einstein equivalent of the Debye temperature;[12] σ represents a reduction of thermal disorder from kT because as $T\rightarrow\infty$, $E_u(T,X)\rightarrow T/\sigma$; and $X=\langle q^2\rangle_x/\langle q^2\rangle_0$ is a measure of structural disorder. However, the definition of structural disorder in the molecular solid C_{60} should be not only the site disorder but also the orientational disorder of the C_{60} molecules. As we will see in the following, the orientational disorder of the C_{60} molecules affects the Urbach-tail parameter E_u. In this paper, we study the optical-absorption edge and its relation to both the thermal and structural disorder in C_{60} films in a wide temperature range of 8.8–470 K.

II. SAMPLE AND EXPERIMENT

C_{60} thin films were prepared by thermal evaporation with a background vacuum 5×10^{-6} Torr. C_{60} powder with 99.98% purity was used as a source and preheated at 250 °C for 8 h to release O_2 gas and toluene from the powder. The source temperature was 400 °C and the substrate temperature was 250 °C. The films were deposited on both Corning 7059 glass and quartz substrates. The sample thicknesses were 1.0–8.5 μm. The films crystallized in the fcc structure at room temperature. The crystalline sizes were 30–47 nm measured by x-ray diffraction patterns.[13]

Photothermal-deflection spectroscopy (PDS) (Ref. 14) and transmission spectroscopy were used to study optical-absorption spectra. For PDS measurements, a halogen tung-

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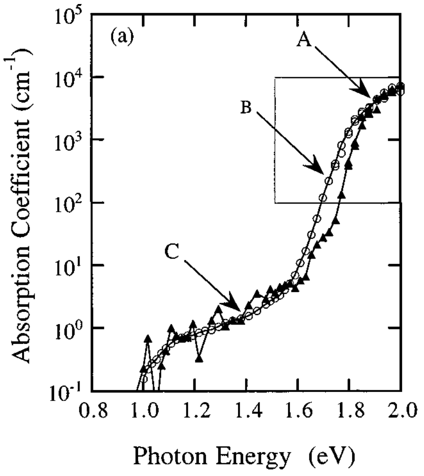
sten lamp and a semiconductor laser LT015MF0 (Sharp Corporation) were used as a pump-light and a probe-beam source, respectively. The probe-beam deflection caused by the photon absorption of the sample was detected by a position-sensitive detector S3929 (Hamamatsu Photonics). At room temperature, perfluorohexane was used as the deflection medium, because perfluorohexane has high transmittance (>90%) in the energy region of 0.6–6 eV and does not dissolve C_{60} films. At 77 K, liquid nitrogen was used as both a cooling and deflection medium. There were two layers of liquid nitrogen in the glass cryostat. The outer nitrogen reservoir suppresses the bubbling of the N_2 gas, and the inner liquid nitrogen works as the deflecting medium. The sensitivity of the PDS system was about $\alpha d = 5\times10^{-6}$ and 5×10^{-5}, at 293 and 77 K, respectively.[15] For transmission spectroscopy, the sample was mounted in vacuum and the measurements were carried out in a wide temperature range of 8.8–470 K. In order to measure the absorption coefficient from 10^1 to 10^3 cm^{-1}, 5- and 8.5-μm-thick samples were used.

III. EXPERIMENTAL RESULTS

The optical-absorption spectra for a group of C_{60} films with thickness of 1.3, 2.4, 2.8, 5.0, and 8.5 μm were measured at room temperature by PDS. All the films were made in the same deposition chamber under the same conditions except a varied deposition time. We found the value of the Urbach tail parameter E_u of 36 ± 1 mV does not depend on the thickness in the films that have been measured. This means that the optical absorption is a bulk property of those polycrystalline C_{60} films. Furthermore, we measured the absorption spectrum of a single-crystal C_{60} sample (size 1 mm^3), and found an E_u of 43 meV, larger than the 36 meV of the C_{60} film. The sample was transferred from the other laboratory. As we know, the PDS technique is very sensitive to the surface conditions; the larger E_u value from this single-crystal C_{60} sample is more likely due to rough surface contribution. Therefore, we believe that the absorption Urbach tail E_u of 36 ± 1 mV in the C_{60} polycrystalline films originates from the optical transitions within the C_{60} molecular solid, not from the surface, interface, or grain boundaries.

The temperature dependence of the optical-absorption edges was measured by both PDS and transmission spectroscopy for two C_{60} films. Figure 1(a) shows the optical-absorption spectra of a 5-μm-thick C_{60} film measured by the PDS technique at 77 and 293 K. In the high-energy side of the absorption spectra, the PDS data are normalized to the transmission data. The high noise level at 77 K originated from both the rough surface of the film and the glass substrate. The characteristic absorption regions are denoted as *A*, *B*, and *C*. In region *A*, the optical gap E_o can be deduced according to Eq. (2). In region *B*, the Urbach parameter E_u can be deduced according to Eq. (1). $E_o = 1.7$ and 1.65 eV and $E_u = 30$ and 37 meV were obtained at 77 and 293 K, respectively. In region *C*, the subband-gap absorption induced by impurities was observed at both temperatures. In addition, an absorption shoulder near 1.7 eV is seen at 77 K. This absorption has been observed by photoacoustic spectroscopy, and explained by the h_u-t_{1u} transition in single-crystalline C_{60}.[16] These PDS results in Fig. 1(a) again prove that the absorption edge of the polycrystalline C_{60} films is identical to that of single-crystal C_{60}. In order to study the temperature dependence of the absorption edge in more detail, we concentrated on the fundamental transition region and the exponential tail indicated by the box in Fig. 1(a). We plotted the results from a 8.5-μm-thick C_{60} film measured by transmission spectroscopy in Fig. 1(b). The sample temperatures were 8.8, 50, 110, 150, 200, 250, 292, 320, 370, 420, and 470 K, respectively. The 150-, 110-, 50-, and 8.8-K curves overlap.

According to the data shown in Figs. 1(a) and 1(b), we calculated the Tauc optical gap E_o and the Urbach tail parameter E_u following Eqs. (1) and (2), and plotted the results in Figs. 2(a) and 2(b). One can see the gradual decrease of E_o and the increase of E_u with increasing temperature. We evaluated the changes ΔE_o and ΔE_u with measurement temperature and found a good mirror symmetry, which implies



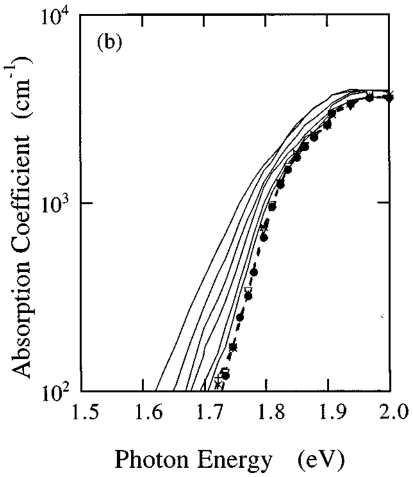


FIG. 1. (a) Optical absorption measured by PDS and transmission of a 5 μm-thick C_{60} film at 77 and 293 K. The solid dots are transmission data, the solid triangles and open circles are PDS data at 77 and 293 K, respectively. Three characteristic absorption regions are denoted as *A*, *B*, and *C*. (b) Temperature dependence of the optical-absorption edge measured by transmission spectroscopy of a 8.5 μm-thick C_{60} film. The curves, from bottom to top, correspond to 8.8, 50, 110, 150, 200, 250, 292, 320, 370, 420, and 470 K, respectively. The 150-, 110-, 50-, and 8.8 K curves overlap.

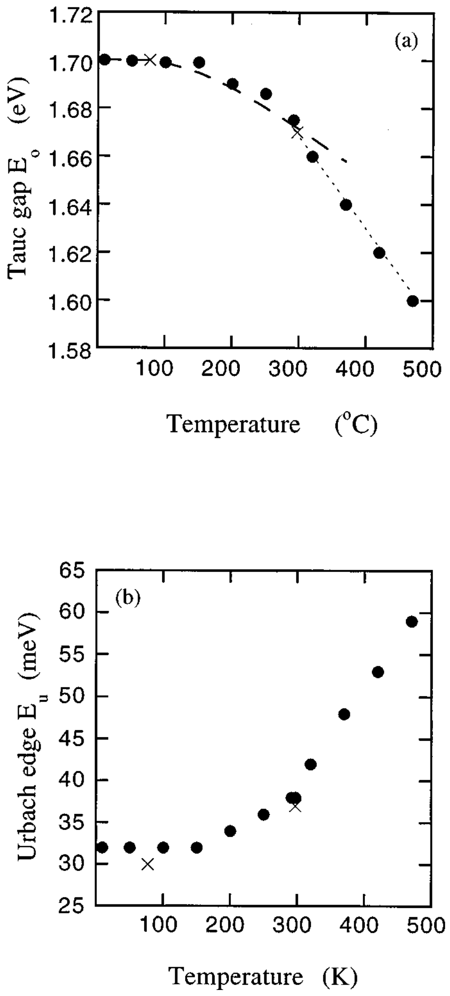


FIG. 2. Temperature dependence of (a) optical gap E_o, and (b) Urbach-tail parameter E_u, data deduced from the curves in Figs. 1(a) (crosses) and 1(b) (solid dots), respectively.

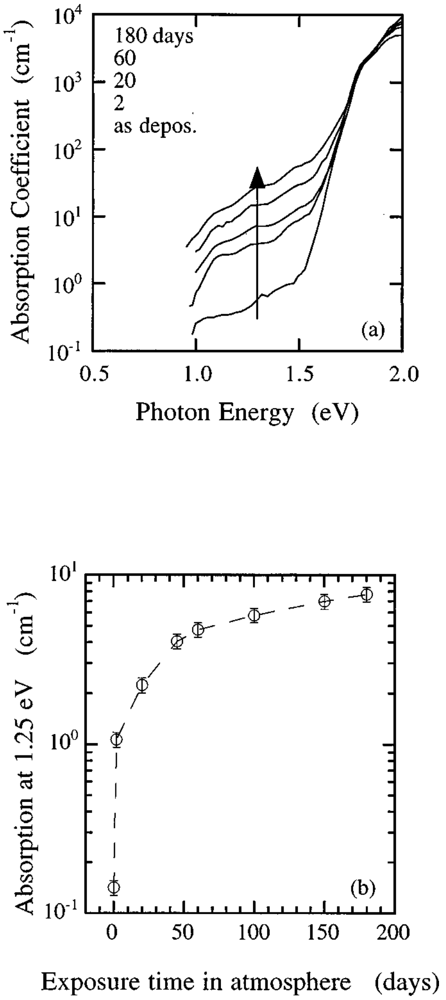


FIG. 3. Air-exposure time dependence for a 1.3-μm-thick C_{60} film at room temperature, (a) absorption spectra, and (b) subgap absorption at 1.25 eV.

that a redshift (or reduction in E_o) occurs simultaneously with a broadening of the tail (or an increase in E_u). Interestingly, we found in Figs. 2(a) and 2(b) that there are three temperature regimes for both E_o and E_u: (1) $T < 150$ K, they do not change, obviously; (2) $150 < T < 260$ K, they change gradually; and (3) $T > 260$ K, they change rapidly. In crystalline semiconductors, the temperature effect on the optical-absorption edge can be explained by changes in the electronic band structure due to changes in the total thermal energy and thermal expansion of the solid. In noncrystalline semiconductors, both thermal and structural disorder can affect the optical absorption edge as described in Eq. (3). However, the definition of structural disorder in the molecular solid C_{60} cannot be only the site disorder but is also the orientational disorder of the C_{60} molecules. Moreover, we found that the C_{60} film structure has no changes with deposition temperature from 20 to 300 °C.[17] Therefore, the orientational disorder does not depend on the sample preparation or heat-treatment temperature, but is a function of the measurement temperature. Concerning the temperature effect, the C_{60} molecule can be considered a giant atom, that given the nature of the vibration excitations an Einstein or Debye model can be applied with the C_{60} molecules as the corresponding vibration entities.[1] According to Eq. (3) we fit the data in Fig. 2(a) using an Einstein oscillator $E_o = E_{oo} - 0.1/[\exp(\theta_E/T) - 1]$.[18] For the best fit, two regimes separated at $T \approx 260$ K are needed and shown by the dashed and dotted lines with $\theta_E = 450$ and 250 K, respectively.[19] A much stronger temperature effect is shown in E_o when $T > 260$ K, which is attributed to the free rotation of the C_{60} molecules. Meanwhile, $E_u(T)$ increases from 35 to 59 meV in the temperature range 260–470 K as shown in Fig. 2(b); this is about a 50% increase in E_u.

We further studied the effect of air exposure on the absorption spectra of a 1.3-μm-thick C_{60} film at 293 K and show the results in Fig. 3(a). These spectra were measured at intervals from just after deposition to after 180 days of exposure to air. The magnitude of the sub-band-gap absorption gradually increases with exposure time. This extra absorption can be removed by heat treatment at 200–250 °C in vacuum. We found the same effect after exposing the film to pure oxygen gas.[20] It indicates that the intercalation of O_2 in the C_{60} film during exposure to air gives rise to the extra subgap absorption. However, after subtracting the subgap absorption, the slope of the Urbach tail E_u, 35 meV, does not change with the intercalation of O_2. This means that the Urbach tail parameter E_u is an intrinsic property of the C_{60} material. We plotted the subgap absorption at 1.25 eV as a function of air-exposure time in Fig. 3(b). We found results similar to that of the oxygen-exposure time dependence of the electrical resistivity of oxygen-free single crystal C_{60}.[21] This implies that the oxygen-impurity-induced electronic defect states are located at the middle of the gap. The similarity of the two results can be explained by noting that as the density of the defect states increases, (a) the sub-band-gap absorption increases, while, (b) the Fermi level is pushed further down into the gap, which increases the resistivity.

IV. DISCUSSION AND SUMMARY

The temperature dependence of the optical-absorption edge in C_{60} films was studied by photothermal deflection spectroscopy (PDS) and optical transmission spectroscopy. We found a close correlation between the optical-absorption edge and the degree of orientational disorder of the C_{60} molecules. The three temperature regimes shown in Figs. 2(a) and 2(b) are consistent with the temperature regimes of the orientational disorder,[6–10] that is (1) $T<150\,\mathrm{K}$, the orientation frozen phase, the two low-energy orientations are found to freeze out in a 5:1 ratio; (2) $150<T<260\,\mathrm{K}$, orientational disorder phase; and (3) $T>260\,\mathrm{K}$, free rotation phase. A minimum in the structural disorder correlated to $E_u=30\pm1$ meV was obtained in C_{60} films when $T<150\,\mathrm{K}$. $E_u(T)$ slightly increased from 30 to 35 meV in the temperature range 150–260 K. Whereas, $E_u(T)$ rapidly increased from 35 to 59 meV in the temperature range 260–470 K; this is about a 50% increase in E_u. We explain the strong thermal effect on the optical-absorption edge in relation to the orientational order-disorder and phase transition at 150 and 260 K.[6–10] When we heat the film from liquid-helium temperature, the C_{60} molecules in the crystal phase remain in their low-temperature frozen state until a temperature of ~150 K is reached, where the C_{60} molecules exhibit the orientational disorder phase; upon further increasing the temperature up to 260 K a first-order transition to the fcc structural phase occurs. Meanwhile, the C_{60} molecules are in a free rotation phase, and the rotational, librational, and the intermolecular vibrational degrees of freedom are activated. In addition, extra phonon modes are excited due to fluctuations in the intermolecular distance, the electron-phonon interaction may also be enhanced in the molecule free rotation phase. Due to both the thermal and structural disorder contributions to the Urbach tail parameter E_u, we observed a rapid increase from 35 to 59 meV when $260<T<470\,\mathrm{K}$.

In conclusion, we have observed that the structural disorder, in other words, the orientational disorder of the C_{60} molecules, makes an important contribution to the exponential tail in C_{60} films. We also found that the slope of the Urbach tail does not change with the intercalation of O_2. This implies that the Urbach tail parameter E_u is an intrinsic property of the C_{60} material. More theoretical and experimental study is needed to understand the origin of the Urbach tail and its temperature dependence.

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