

Optical absorption spectra of C₇₀ thin films

Wei-ya Zhou,^{a)} Si-shen Xie, Sheng-fa Qian, Tang Zhou, Ri-an Zhao, and Gang Wang
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Lu-xi Qian

Department of Physics, the Central University of Nationality, Beijing 100087, People's Republic of China

Wen-zhi Li

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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Both optical transmission spectroscopy and photothermal deflection spectroscopy are used to determine the spectra of C₇₀ thin films over a wide energy range (0.6–6.5 eV). Based on a molecular orbital model, the optical transitions for the C₇₀ thin film are analyzed. The weak absorption spectra of C₇₀ thin films are similar to that of an amorphous semiconductor. The optical energy gap is derived by a Tauc plot as 1.66 eV. The gap region can be described in terms used for amorphous semiconductors, having features such as an Urbach edge and subgap defect absorption, which are interpreted as a broadening due to disorder or impurities. The effects of the deflection medium on the weak absorption spectra of C₇₀ films are discussed. © 1996 American Institute of Physics. [S0021-8979(96)07413-0]

I. INTRODUCTION

Optical absorption is an important aspect in studying the optical and thermal properties of a material. With the development of efficient techniques for synthesizing C₆₀ and C₇₀,¹ the optical absorption of these materials attracts considerable interest,^{2–10} since it not only provides a characteristic signature of the fullerene but also contains a wealth of information about the energy levels and the electron density of states. From both the electronic and vibrational transitions, structural and compositional information can often be obtained.

Transmission and reflectivity spectroscopies, which are generally used to yield an absorption spectrum, are not suitable for a sample with weak absorption because the minimum of absorption is 10^{–2} for these spectroscopies. However, photothermal deflection spectroscopy (PDS) has been shown to be suitable for measuring weak absorption in thin films for both inorganic and organic materials. Up until now, a lot of investigations on UV/VIS absorption spectra have been carried out for C₆₀ thin films, but less for C₇₀ thin films. It is especially difficult to determine the absorption spectra from the near-infrared to the visible for C₆₀ and C₇₀ thin films. In this paper, the absorption spectra of C₇₀ thin films over a wide range (0.6–6.5 eV) are measured by means of both transmission spectroscopy and PDS, and compared with the PDS of an amorphous semiconductor. The optical transitions and the weak absorption characteristics of C₇₀ thin films are discussed.

II. EXPERIMENT

Commercially available C₇₀ powder (Peking University) with labeled purity of better than 98% was used. The C₇₀ powder was kept in an evacuated quartz tube at about 523 K for 15 h in order to remove residual solvents used during the separation or purification process. This pretreated C₇₀ was

sublimated in a quartz furnace at 735 K onto clean quartz substrates (1 cm × 0.5 cm, thickness 0.8 mm) held at 415 K during deposition in a vacuum of 10^{–8} Pa. A typical flux rate for C₇₀ deposition was about 2 nm/min. The shutter over the substrate was closed while the temperatures of the source and substrates were rising. The thickness of the C₇₀ film was measured by a Dektak IIA profilometer. Raman and IR spectra confirmed that the obtained thin films consisted almost entirely of polycrystalline C₇₀.

A direct transmission method was used to measure the strong UV/VIS transitions by a CARY 2390 UV/VIS/NIR spectrophotometer. The scanning rate was 1 or 0.5 nm/s. The weak absorption spectrum below 2.5 eV (500 nm) was determined by photothermal deflection spectroscopy (PDS). Briefly, the latter technique uses the heating from the weakly absorbed light to deflect a laser probe beam skimming along the surface of the film at the point of illumination. With a position-sensitive detector placed an adequate distance from the interaction region, very weak absorptions can be translated into detectable beam displacements. The wavelength of the absorbed light can be scanned and the absorption as a function of wavelength can be obtained. The PDS data can then be overlapped with the transmission data in the region where the former is near saturation while the latter is near the resolution limit, and a full spectrum is obtained. Because of the high sensitivity of PDS it is possible to measure forbidden transitions as well as defect states that would not be detected by other techniques. Additional details about PDS are given in Refs. 11 and 12. The measurements were performed at room temperature. Silicone oil or alcohol is selected as a deflection medium.

III. RESULTS AND DISCUSSION

The full spectrum of C₇₀ thin film is shown in Fig. 1, which is a plot of log absorbance versus incident photon energy. The vertical axis is essentially the log of the optical density, and the wavelength ranges from 190 nm (6.5 eV) to

^{a)}Electronic mail: ghrao@aphy02.iphy.ac.cn

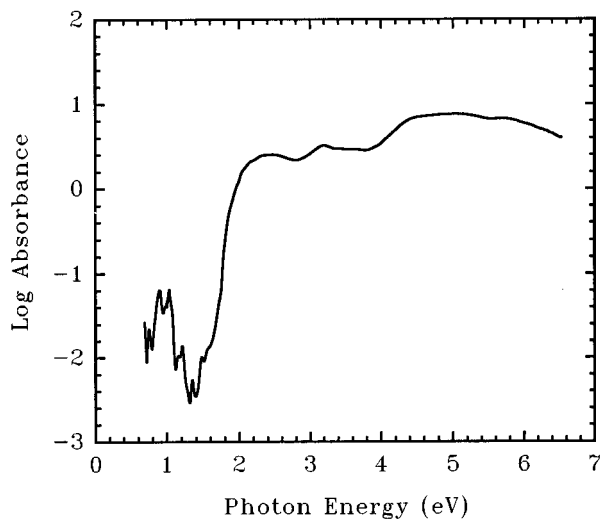


FIG. 1. Optical absorption of a C_{70} thin film.

2400 nm (0.52 eV). The main optical transitions are between 190 nm (6.5 eV) and 550 nm (2.25 eV) and can be measured by standard transmission measurements. An interesting aspect of the PDS spectra is the nature of the weak absorption beyond 550 nm (2.25 eV) where the absorption drops off rapidly.

The spectrum can be separated into three energy ranges: (1) “above gap”: 6.5–2.3 eV (190–540 nm), (2) “near gap”: 2.3–1.6 eV (540–770 nm), and (3) “subgap”: below 1.6 eV (770–2400 nm).

A. Above gap region

For the first region, the UV/VIS spectra with a linear scale for the absorbance are shown in Fig. 2 for two C_{70} thin films with different thicknesses (solid line: 1600 Å, dashed line: 400 Å). For a standing film, since the expression for transmittance is very complicated with two reflectances: one for the film-air interface and the other for the film-substrate

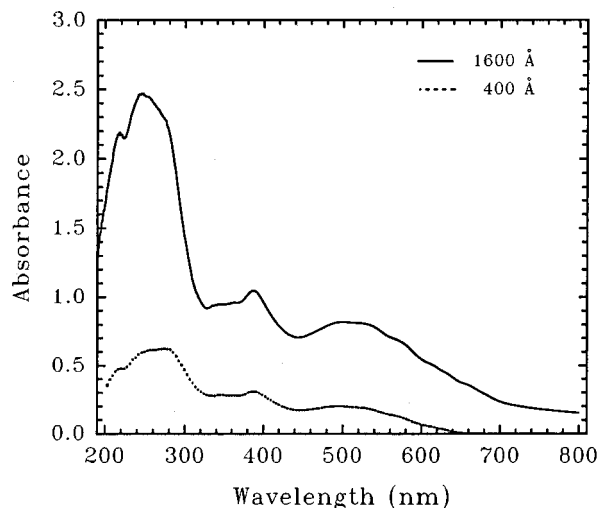


FIG. 2. UV/VIS spectra of two C_{70} films.

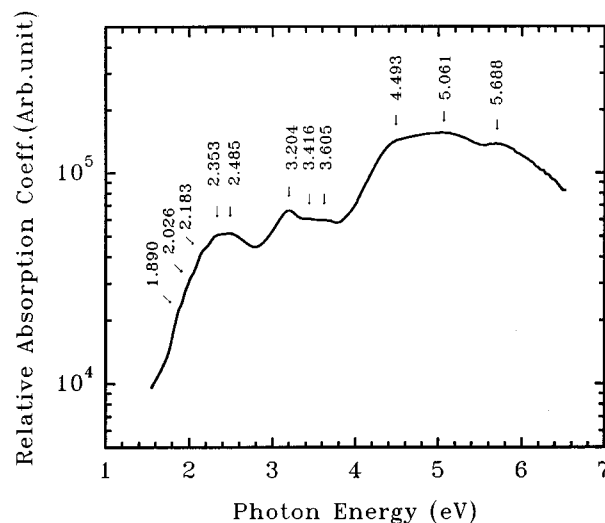


FIG. 3. Relative absorption coefficient vs photon energy for a C_{70} thin film.

interface, it is difficult to determine an absolute absorption coefficient of the film from the measured transmission. Therefore, we define here a relative absorption coefficient α , as $[-\log(I/I_0)/d]$, where I/I_0 and d represent transmittance and thickness of a thin film, respectively. Figure 3 shows the relative absorption coefficient versus photon energy.

Absorption by C_{70} thin film begins with a weak onset band at about 700 nm (1.771 eV), followed by a series of very weak peaks at 656 nm (1.890 eV), 612 nm (2.026 eV), 568 nm (2.183 eV), and 527 nm (2.353 eV) superimposed on a gradually rising continuum leading to a stronger maximum at 499 nm (2.485 eV). A broad minimum covers the blue-violet region. A maximum of intermediate strength appears in the near-ultraviolet region at 387 nm (3.204 eV), followed by two very weak peaks at 363 nm (3.416 eV) and 344 nm (3.605 eV). The ultraviolet region is dominated by very strong broad bands peaking at 276 nm (4.493 eV), 245 nm (5.061 eV), and 218 nm (5.688 eV), respectively.

The main absorption peaks of the C_{70} film have shifted to longer wavelength with respect to the spectrum of the C_{70} molecule in a solution:¹⁰

Liquid phase (C_{70} in hexane): 215 236 378 469 nm,
Solid phase (C_{70} solid thin film): 218 245 387 499 nm.

Overall we observe a striking similarity of the absorption in the C_{70} solid film and C_{70} in hexane,¹⁰ which is consistent with the view that solid C_{70} is nearly an ideal molecular solid. This indicates that the Van der Waals and Coulomb interactions between C_{70} molecules are indeed weak in the solid film, and the molecularity is reserved for the electronic

TABLE I. Dipole-allowed transitions for the C_{70} molecule.

$A'_1, A'_2 \leftrightarrow E'_1$	$E'_1, E'_2 \leftrightarrow E'_2$	$A'_1 \leftrightarrow A'_2$	$A'_2 \leftrightarrow A'_1$
$A''_1, A''_2 \leftrightarrow E''_1$	$E''_1, E''_2 \leftrightarrow E''_2$	$E'_1 \leftrightarrow E''_1$	$E'_2 \leftrightarrow E''_2$

energy structure of the C_{70} solid, although the absorption peaks are red shifted from the molecular C_{70} in hexane due to the stronger interaction between molecules in the solid state. The same similarity has been observed in the spectra of solid C_{60} and the solution of C_{60} .¹³

Since the C_{70} molecule with its ellipsoid “rugby ball” shape has the lower symmetry D_{5h} , compared to the higher symmetry I_h , of spherical C_{60} molecules, there are only up to twofold degenerate states in C_{70} and the electronic energy levels for the solid C_{70} would exhibit an abundant distribution of structure. The agreement between the experimental results¹⁴ and the theoretical analysis^{15,16} confirms that the lowest unoccupied bands in C_{70} are derived from a nondegenerate A_1'' level and a twofold degenerate E_1'' level. But calculations by various kinds of models gave different energy levels and their order for both the LUMO (lowest unoccupied molecular orbital) and the HOMO (highest occupied molecular orbital). Therefore, due to the complication of the electronic energy levels in solid C_{70} it is difficult to assign the transitions for a C_{70} thin film. Here, we estimate the transition behavior exclusively based on the relative energy levels of C_{70} reported in Ref. 15. According to the dipole selection rules (listed in Table I), which are obtained from group theory for the D_{5h} symmetry group, and assuming that the energy gap between the HOMO and the LUMO is 1.66 eV given in this experiment (see below), the energies for the dipole-allowed transitions are then derived. By comparing with the optical spectra (Fig. 3), we tentatively assign $A_2'' \rightarrow A_1'$ to the 2.485 eV transition region; $A_2' \rightarrow A_1''$ to the 2.353 eV; $A_2', E_1'' \rightarrow E_1'$ to the 3.204 eV; $E_1'' \rightarrow A_2'', E_2' \rightarrow E_1'$ to the 4.493 eV; $E_1'' \rightarrow E_2'', E_2' \rightarrow E_2'$ to the 5.061 eV, and $E_1' \rightarrow E_2', E_2'' \rightarrow E_2'$ to the 5.688 eV regions.

B. Near-gap region

The PDS spectrum of a 1 μm thick C_{70} film is shown in Fig. 4(a) with a plot of relative absorption coefficient versus photon energy. Alcohol was taken as the deflection medium. The figure for this region is highly reproducible for various samples with different thicknesses. The spectrum can be divided into three regions: A, B, and C, as shown in Fig. 4. Region A, where the relative absorption coefficient α , is proportional to the power of the incident photons of energy, $h\nu$, is called a “high” absorption region. Region B is an “exponential” absorption region, where α is proportional to the exponent of $h\nu$. Region C denotes the “subgap” absorption dominated by transitions from extended valence band states to the defect states or from the defect states to extended conduction band states. Here, regions A and B are classified as “near-gap” absorption region.

The spectrum of the C_{70} thin film [Fig. 4(a)] is similar to that of amorphous semiconductor films. In order to make a comparison between these two kinds of film, the absorption spectrum of an amorphous silicon/silicon nitride multilayer film ($a\text{-Si:H/SiN}$, 1.6 μm thickness) is measured by PDS, and also shown in Fig. 4(b). Alcohol is chosen as the deflection medium. For region A ($h\nu \sim 1.8\text{--}2.0$ eV) in the spectrum of the C_{70} film, therefore, the optical gaps can be determined by using the Tauc equations^{17,19} which are usually adopted

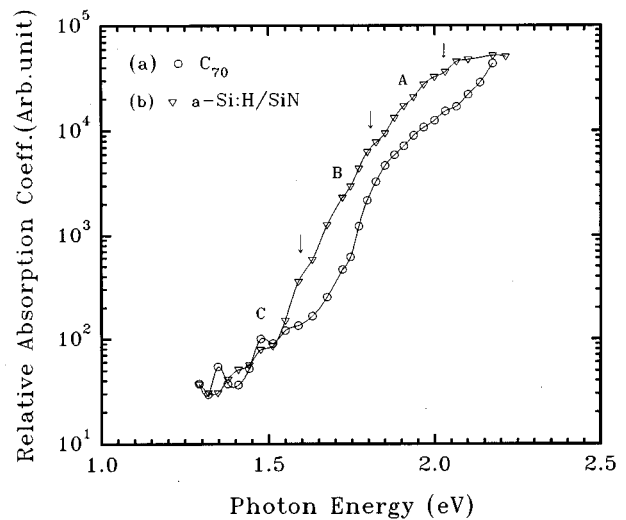


FIG. 4. Visible and near-IR spectrum determined by PDS. (a) C_{70} thin film; (b) $a\text{-Si:H/SiN}$ multilayer film.

for semiconductors. For the quadratic relationship, usually, three types of Tauc plots [Eqs. (1)–(3)] are tried:

$$(\alpha h\nu)^{1/2} = B_1(h\nu - E_{\text{opt}}), \quad (1)$$

$$(\alpha)^{1/2} = B_2(h\nu - E_{\text{opt}}), \quad (2)$$

$$(\alpha/h\nu)^{1/2} = B_3(h\nu - E_{\text{opt}}), \quad (3)$$

where E_{opt} is the optical energy gap, $h\nu$ is the energy of the incident light, and B is a constant related to the properties of the material. Equation (1) is used mainly for amorphous semiconductors.

Figures 5 and 6 show the Tauc plots for a C_{70} thin film and an $a\text{-Si:H/SiN}$ multilayer film, respectively. The E_{opt} s derived from the three different Tauc plots [Eqs. (1)–(3)] are listed in Table II. Because each plot corresponds to a straight line in the same energy region ($h\nu \sim 1.8\text{--}2.0$ eV) with a little difference in the quality of fitting, the plot with Eq. (1) will

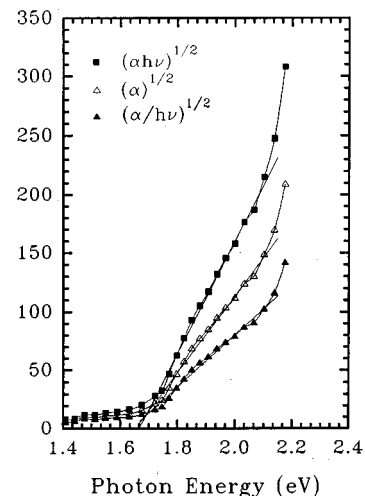


FIG. 5. Tauc plots for the C_{70} thin film.

be reasonably used to estimate E_{opt} for C_{70} thin films as it is for an a -Si:H/SiN multilayer film. From fitting the data to Eq. (1), the parameter B can be obtained, which is in inverse proportion to the width of the conduction band and the valence band tail.¹⁸ The B is about 2.1×10^5 and 6.2×10^5 for the C_{70} thin film and a -Si:H/SiN multilayer film, respectively.

Theoretical analysis indicates that the LUMO of C_{70} consists of two orbitals: the nondegenerate A_1'' orbital and the twofold degenerate E_1'' orbital, which are distinctly separated by a small energy gap.¹⁶ While the symmetries of LUMO and LUMO+1 are reversed in the quantum-chemical calculations,²⁰ the more accurate density-functional calculations²¹ produce the same ordering as in the tight-binding results.¹⁶ Moreover, the HOMO of C_{70} are derived from A_2'' and E_1'' with a small energy gap¹⁶ or with the same energy.¹⁵ It is too complicated to fully understand the nature of the electronic structure of C_{70} . According to Ref. 16, the HOMO–LUMO dipole transition is a symmetry-forbidden one. About 0.3 eV above the HOMO–LUMO gap is the lowest allowed transition occurring at 1.9 eV between the HOMO (A_2'') and the LUMO+1 (E_1''). The HOMO–1 (E_1'')–LUMO (A_1'') transition also occurs at about the same energy. This is not in agreement with the lowest transition in the absorption spectrum by PDS, which occurs at the energy of 1.66 eV. However, since the effects of disorder are found in the C_{70} thin film, E_{opt} is identified with the energy of 1.66 eV which is close to some other calculated HOMO–LUMO gaps: 1.65 eV,²¹ 1.68 eV,²² and 1.76 eV.²³ But there are larger differences among the various experimental results for the energy gap of solid C_{70} , e.g., 1.6 eV by photoelectron spectroscopy,²⁴ 1.25 eV by variable-angle spectroscopic ellipsometry,²⁵ 3.75 eV by photoelectron spectroscopy and inverse-photoelectron spectroscopy.²⁶ The obtained value of E_{opt} indicates that the C_{70} film is a semiconductor as the C_{60} film.

The disorder in C_{70} films can be represented by the Urbach energy, which is exhibited in the PDS. It is the disorder which results in the difficulty in determination of the energy

TABLE II. E_{opt} (eV) derived by Tauc plots.

Tauc plots	C_{70}	Film a -Si:H/SiN
$(\alpha h\nu)^{1/2}$	1.66	1.68
$(\alpha)^{1/2}$	1.65	1.66
$(\alpha/h\nu)^{1/2}$	1.64	1.64

gap for C_{70} thin films. For region B in Fig. 4, the relation between α and $h\nu$ can be characterized by the expression:

$$\alpha = \alpha_0 \exp(h\nu/U), \quad (4)$$

where U is the ‘‘Urbach energy’’ which is interpreted as a broadening of the intrinsic absorption edge due to disorder and related to the transitions from the extended valence band states to the localized states at the conduction band tail. The larger the value of U , the greater the compositional, topological, or structural disorder. For the C_{70} thin film this energy is 55 meV, which is comparable to the value of 69 meV obtained for an a -Si:H/SiN multilayer film. There are several possible origins for the disorder in C_{70} films: (1) The surface of the film is inevitably contaminated by impurities or intercalated by oxygen, since the sample has been exposed to air for a time. (2) It is easy to produce structural defects such as stacking faults or irregularly oriented microcrystal boundaries. (3) Since the molecules of C_{70} rotate highly at room temperature, domains could be introduced which might destroy the long-range order in films. It is these disorders that give rise to the band tail and subgap defect states.

C. Subgap region

The absorption behavior in the C_{70} film below 1.6 eV is more complicated. In region C of Fig. 4(a) the absorption shoulder at about 1.5 eV is attributed to the transition between subgap states, which reflects the density and distribution of subgap states. The shoulder is strikingly similar to the silicon dangling bond absorption in a -Si:H/SiN which is shown in Fig. 4(b). It is plausible that this shoulder is due to the existence of the carbon dangling bond, i.e., an unpaired electron orbital. Given the closed structure of C_{70} , the most likely interpretation is that the films are bimodal in nature, comprised of both C_{70} molecules and an interstitial material. The unpaired spins could be associated with pregraphitic fragments which are known to have radicals, and probably have hydrocarbons incorporated. This latter aspect might account for C–H stretching overtones. The possible presence of C_{60} on the order of a few percent as well as the origins for defect formation discussed above may also contribute to the subgap features.

Absorption below 1.4 eV is increasing. There are resonances near 0.9 and 1.0 eV which is typically a region of vibrational overtones. These peaks may be C–H and O–H overtones. In order to further elucidate this feature, we have measured the PDS of the quartz substrate using alcohol and silicone oil as the deflection media, respectively, and also measured the PDS of the C_{70} film in these deflection media (Fig. 7). It is observed that the absorption of C_{70} film is

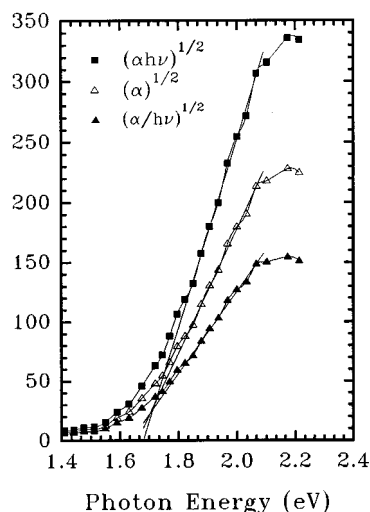


FIG. 6. Tauc plots for the a -Si:H/SiN multilayer film.

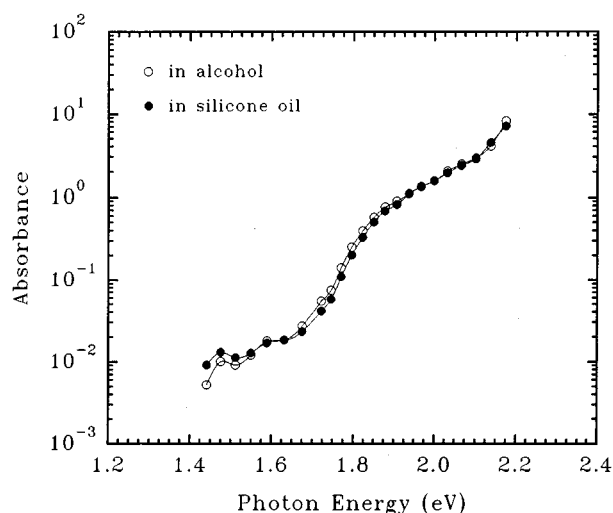


FIG. 7. PDS of the C_{70} thin film in different deflection media.

covered on the whole by the absorption of organic medium below 1.4 eV (alcohol) or 1.1 eV (silicone oil). It is essential in this case to select a transparent deflection medium with high index-of-refraction. Alcohol and silicone oil are chosen as the medium because C_{70} molecule is dissolvable in carbon tetrachloride (CCl_4) which is transparent between 0.4 and 2.4 μm and is usually used as a good medium. We have also attempted to use some other organic solutions, but failed to find a suitable one as a very good medium for this measurement.

By comparison of the absorptions of C_{70} films with alcohol or silicone oil as deflection media, the latter seems better than the former as a medium. Figure 7 indicates that the influences of medium upon the absorption of C_{70} film in the near-gap region could be neglected in the present PDS measurement.

IV. CONCLUSIONS

The optical absorption spectra of C_{70} thin films from 0.6 to 6.5 eV are measured by the combination of PDS with conventional transmission spectroscopy. The similarity in the spectra of the C_{70} thin film and the solution of C_{70} has been observed, although the absorption peaks for the C_{70} thin film are red shifted, compared to those for the molecular C_{70} in an organic solvent. The red shift of the absorption peaks is attributed to the stronger interaction between molecules in the solid state. For the polycrystalline C_{70} thin film, several features in the weak absorption region are strikingly similar to amorphous semiconductors. The exponential Urbach tail is attributed to the disorder due to unknown impurities or structural defaults. The absorption shoulder appears in the subgap region, which may be an evidence for the existence of carbon

dangling bonds. The effects of the deflection mediums (alcohol or silicone oil) below 1.4 eV are significant and thus it is essential to select a suitable medium. By using a Tauc plot the optical energy gap E_{opt} of the C_{70} thin film is determined as 1.66 eV. Therefore, it is interesting that the C_{70} film exhibits a semiconductorlike behavior in optical absorption properties and yet retains a molecular character. C_{70} thin films might provide an opportunity to study the "crossover" from molecular to extended systems.

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