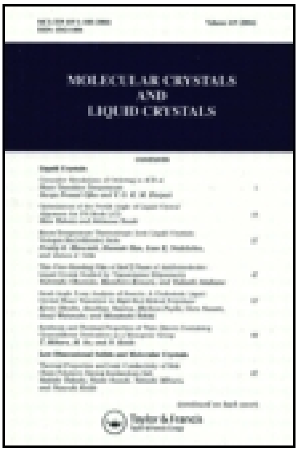

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Properties of Electronic Excited States of C_{60} Thin Films as Seen from Photoconductivity and Luminescence Behavior: Dependence on Excitation Wavelength and Temperature

Nobutsugu Minami [a], Said Kazaoui [a] & Robert Ross [a] [b]

[a] National Institute of Materials and Chemical Research, AIST 1-1 Higashi, Tsukuba, Ibaraki, 305, Japan

[b] N. V. Kema, Utrechtseweg, 6812 AR, Arnhem, The Netherlands

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PROPERTIES OF ELECTRONIC EXCITED STATES OF C_{60} THIN FILMS AS SEEN FROM PHOTOCONDUCTIVITY AND LUMINESCENCE BEHAVIOR: DEPENDENCE ON EXCITATION WAVELENGTH AND TEMPERATURE

NOBUTSUGU MINAMI, SAID KAZAOUI, AND ROBERT ROSS*
National Institute of Materials and Chemical Research, AIST
1-1 Higashi, Tsukuba, Ibaraki 305, Japan
*On leave from N.V.KEMA, Utrechtseweg, 6812 AR Arnhem,
The Netherlands

Abstract Photoconductivity and its temperature dependence have been measured for both oxygen-exposed and nonexposed C_{60} thin films. A constant activation energy for different wavelengths, together with the insensitivity of luminescence emission spectrum to excitation energy, suggests a molecular excitonic nature of solid C_{60}'s electronic states. Luminescence excitation spectra show that emission efficiency is higher for the excitation of forbidden states than allowed states. A turning point at 250-260K has been found in a luminescence vs. temperature curve and is discussed in relation to the phase transition from fcc to sc.

INTRODUCTION

The uniqueness of fullerene lies in its molecular shape and structure that bring about exceptional behavior such as the fast molecular rotation in the solid state[1] and the phase transition near room temperature.[2] These phenomena, combined with π electron conjugation around the entire ball surface, result in a variety of optical and electrical properties that are considerably different from those of conventional molecular solids.

We have been working on photoconductivity of fullerene since the discovery of sizable photocurrent in vapor deposited C_{60} thin films.[3] In the present study, luminescence in combination with photoconductivity was employed to obtain an insight into excited state properties of this new carbon allotrope. These two phenomena are closely interrelated with respect to excitation relaxation processes, and their combined analysis is believed to give us new information that is essential for assessing potential applications of fullerene.

It is well documented that electrical properties of C_{60} are strongly affected by oxygen: decreases in dark- and photocurrent by 3 to 4 orders of magnitude were reported.[4,5] Although these recovered after driving out absorbed gas by heating in vacuum, one-hundred percent recovery has not been achieved at the present stage. In our experimental procedure, C_{60} thin films are vapor-deposited in high vacuum and their electrical properties are measured without exposure to air, to be referred to as "in situ" measurements here. This precaution is important in revealing the disturbance-free electrical properties of fullerene.

A number of luminescence studies on C_{60} thin films have been made.[6-8] However, there are no reports so far on the luminescence excitation spectrum, despite its importance as a tool for obtaining better understanding of excitation relaxation processes. The luminescence excitation spectra of C_{60} thin films reported in this paper have revealed several new features such as a wavelength dependent luminescence quantum efficiency. We also found that luminescence intensity as a function of temperature showed a turning point at 250-260K, the well-known phase transition temperature. This is the first example of a UV/Vis optical property affected by the phase transition, opening up a new research area concerning the structure-property relationship of solid fullerene.

EXPERIMENTAL

Purified C_{60} powder from a commercial source (Shinku Yakin) was used as received, its purity 99.9% being established by HPLC. Evaporation was carried out in a vacuum of 10^{-5} Pa. Controlling the temperature to 340°C of an aluminum or a quartz crucible containing C_{60} powder yielded an evaporation rate of about 0.4 nm/min. Quartz or sapphire plates were used as substrates, which were heated to 110°C to improve film quality.

For electrical measurements, a pair of coplanar gold interdigitated electrodes were deposited on substrates. The electrode gap was 0.1 mm and the length 100 mm. Electrical connection was made by pressing a strip of phosphor bronze onto the gold electrode. This setup, together with a quartz light pipe introducing monochromatic illumination into the vacuum chamber, enabled in situ electrical measurements, where samples could be tested without exposure to air.

To measure photocurrent spectra, a xenon lamp and a monochromator (Nikon G-250) were used together with a neutral density (ND) filter. Computer-controlled rotation of the ND filter kept the number of photons impinging on samples constant irrespective of excitation wavelength, yielding directly photocurrent spectra corrected to a constant photon flux (typically 10^{14} $cm^{-2}s^{-1}$).

Samples for luminescence measurements were inevitably exposed to air for short time during their transfer from the vacuum chamber to a cryostat (Oxford DN1704). Possible effects of absorbed oxygen were checked by observing a change induced by baking thin films in vacuum in the cryostat.

Luminescence emission and excitation spectra were measured with a spectrofluorometer (JASCO FP777) operated in its most sensitive mode. Appropriate cut filters were inserted to eliminate stray emission lines. For temperature dependence measurements, care was taken to ensure that steady-state for both luminescence intensity and temperature was reached by allowing sufficient time before reading each set of data.

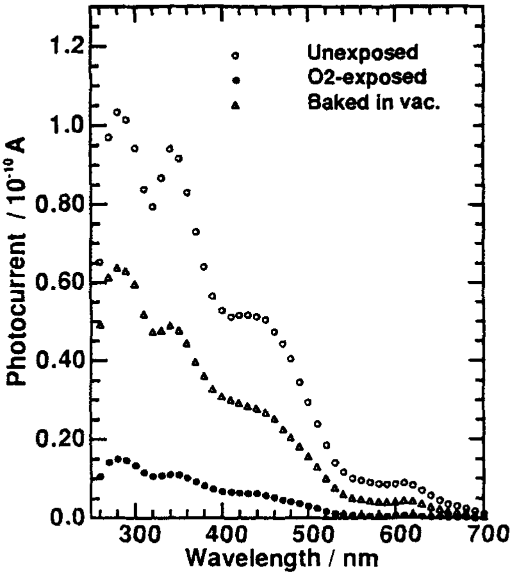

FIGURE 1 Photocurrent spectra of a 20 nm thick C_{60} film after various treatment histories.

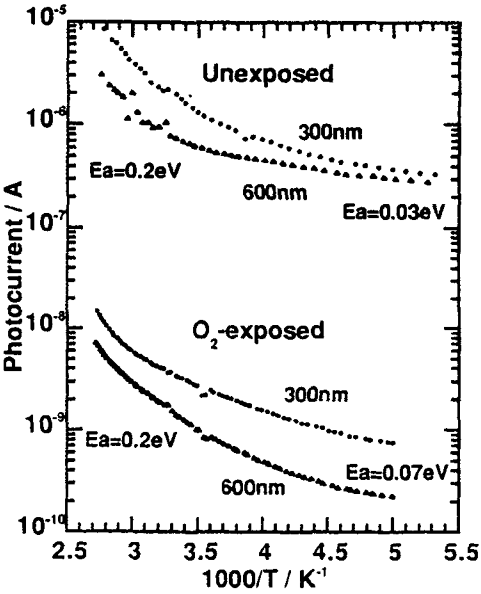

FIGURE 2 Temperature dependence of photocurrent of a 200 nm thick C_{60} film under various conditions.

RESULTS AND DISCUSSION

Effect of Oxygen on Photoconductivity

As reported in our previous paper, photoconductivity is greatly quenched by introduction of oxygen, while nitrogen caused no such an effect.[5] The evacuation of the sample chamber alone did not recover photocurrent, indicating that the effect of oxygen cannot be easily removed at room temperature. By heating sample at around 110°C for at least a few hours, recovery of 50-70% could be attained. At the present stage, however, there is no guarantee that the oxygen effect is 100% reversible. This confirms the vital importance of in situ electrical measurements for assessing the properties of fullerenes, as being pursued by this group. The decrease of photocurrent was dependent on film thickness; thicker films underwent larger decrease.

Figure 1 shows the spectral dependence of photocurrent at room temperature after different treatment histories; in situ, in vacuum after exposure to oxygen, and in vacuum after baking for a few hours. Except for a change in magnitude, the spectral shape did not show a significant variation accompanying these treatments, indicating that the effect of oxygen here is not such a kind that causes the deterioration of electronic states in C_{60} thin film.

Temperature Dependence of Photoconductivity

The temperature dependence of photocurrent was measured to obtain an insight into photocarrier generation processes. In Figure 2 are shown Arrhenius plots of photoconductivity under various conditions such as different excitation wavelengths and with or without oxygen-exposure. Wavelengths of 300 nm and 600 nm correspond to allowed and forbidden transition, respectively. The important result here is that the plots for the two wavelengths show nearly the same slope, meaning that activation energy necessary for photocarrier generation is invariant for the allowed and forbidden excited state. One can construct a scheme where different excited states, whether allowed or forbidden, relax to the same low lying state from which charge carrier generation occurs.

We might consider the high temperature portion of the Arrhenius plots, i.e., an activation energy of ca. 0.2 eV, as reflecting the more intrinsic part of a photocarrier generation process. This, together with an energy gap of 1.9 eV as obtained from the intrinsic dark conductivity activation energy of C_{60} single crystal,[9] suggests that the state from which charge separation occurs is about 1.7 eV above ground state. This is consistent with luminescence emission edge around 700 nm (vide infra), meaning that light emission and charge separation are competing processes occurring from the same state. Detailed discussion on this matter, however, should await more elaborate experiments such as the temperature dependence of effective mobility in polycrystalline C_{60} thin film and the simultaneous measurement of luminescence and photoconductivity.

It is also shown in Figure 2 that the activation energy for photoconductivity was not appreciably changed by oxygen exposure. This might mean that the effect of oxygen is not so significant in a photocarrier generation step, but most serious in a carrier transport step. It is interesting to note that the radical anion of C_{60} electrolytically produced in solution was rapidly destroyed by oxygen.[10] This suggests that a carrier conduction state in solid C_{60} is its anion itself, which would be most seriously influenced by oxygen.

Relationship between Photocurrent and Absorption Spectra

The shape of the photocurrent spectrum is found to vary for different film thickness. As shown in Figure 3, for a 25 nm thick C_{60} film, the spectral dependence approximately follows the absorption spectrum (symbatic relationship), while antibatic relationship was found for a 200 nm thick film, where a photocurrent dip corresponds to an absorption peak for $\lambda < 400$ nm.

This kind of behavior is often observed for photocurrent spectra of molecular thin films. Giro et al. proposed that a similar behavior for C_{60} sandwich cells can be explained by a bimolecular recombination model,[11] where generated carriers are mostly quenched by electron-hole recombination. This interpretation seems quite valid for the present case, because their expressions describing the wavelength and thickness dependence of photocurrent are found to give an excellent fit to the photocurrent spectra in Figure 3. The fact that the photocurrent was approximately proportional to the square root of light intensity supports this view. It should be noted that for surface-type configuration as used in the present study, carriers are more susceptible to bimolecular recombination than for sandwich-type configuration, as pointed out by Gailberger and Baessler.[12]

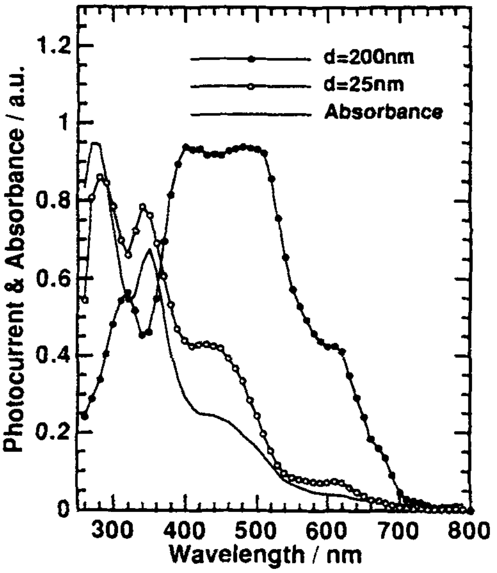

FIGURE 3 Photocurrent spectra for a 200 nm and a 25 nm thick C_{60} film and an absorption spectrum.

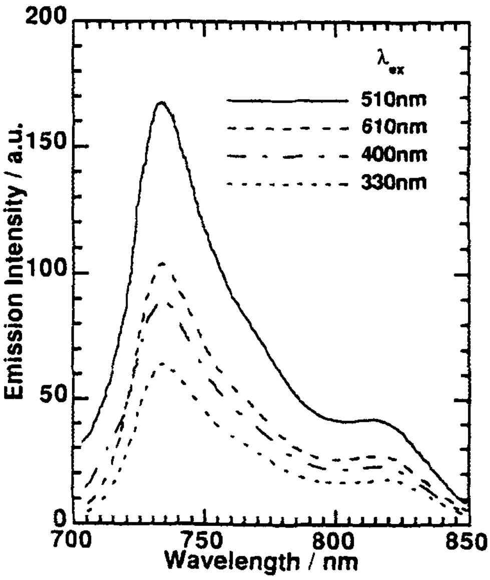

FIGURE 4 Luminescence emission spectra at 77K for different excitation wavelengths.

Luminescence Emission Spectra

Luminescence emission spectra were measured for various excitation wavelengths. The results are shown in Figure 4. The overall shape and the peak position around 735 nm agree with those of previous reports.[6-8] The important feature here is that the shape of the emission spectra does not change depending on the excitation energy. This means that every excited state involved, whether allowed or forbidden, relaxes to the same level from which the emission occurs. This situation is similar to what has been observed in the photocarrier generation process.

It should be added that the luminescence measurements were all performed for samples that were once exposed to air during transfer from the deposition chamber to the cryostat. So these were not "in situ" measurements. To check the effect of oxygen, a C_{60} film was baked at 220° C for 10h in vacuum, increasing the emission by about 40%. One can say that oxygen quenches C_{60}'s luminescence to some extent but the effect is not as large as for photoconductivity.

Luminescence Excitation Spectra

When luminescence is used as an optical probe of new materials, both an emission and an excitation spectrum should be measured as an indispensable and complementary set of data. Comparison of the two and with the absorption spectrum give essential insights into excited state properties. To the best of our knowledge, the luminescence excitation spectrum given in Figure 5 is the first one reported for solid C_{60}. For a small film thickness such as 20 nm, there are roughly three regions of important spectral features. The first is a peak at 350 nm coinciding with

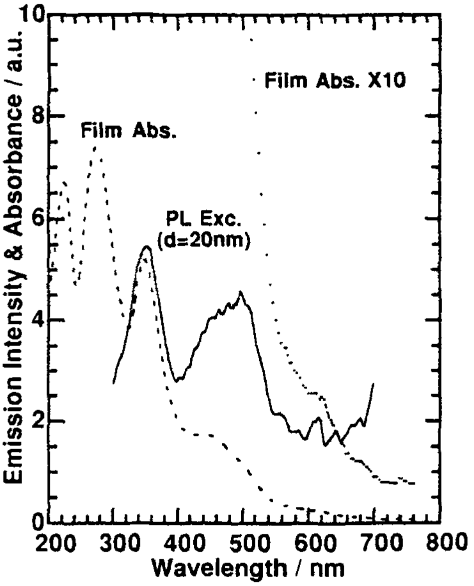

FIGURE 5 Luminescence excitation spectrum of a 20 nm thick C_{60} film at 77K and an absorption spectrum of C_{60} thin film.

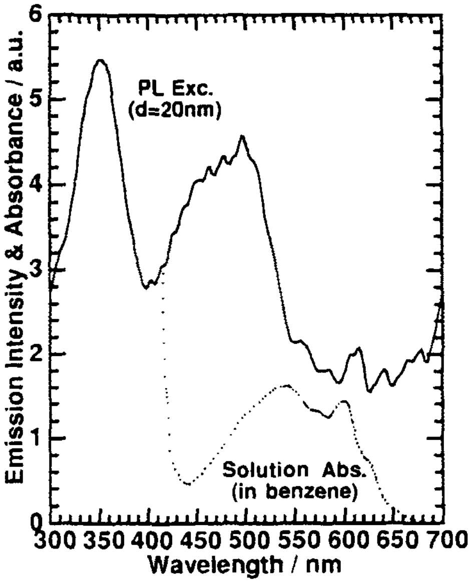

FIGURE 6 Luminescence excitation spectrum as in FIGURE 5 and an absorption spectrum of benzene solution of C_{60}.

the allowed absorption peak, the second a peak at 440-520 nm corresponding to the solid-state specific absorption, and the third fine structures at 550-680 nm reflecting phonon replicas of the HOMO-LUMO forbidden transition. The small structures at 450-500 nm are an experimental artifact caused by xenon lamp's sharp spectral lines that persisted even after a correction procedure.

Comparison of the excitation spectrum with absorption shows that the relative ratio of luminescence to absorption is larger at 440-520 nm than at 350 nm, meaning that quantum efficiency is higher at the solid-state specific absorption. This suggests that the excited states that are originally forbidden but somehow allowed by the intermolecular interaction in the solid state suffer less quenching than do the originally allowed excited states. When the film became thicker, the luminescence excitation spectrum was dominated by a peak at 520 nm with small dip at 350 nm. This kind of thickness effect may be partly explained by different penetration depths for each wavelength. For a more satisfactory explanation, however, measurements with gradual increases in thickness may be necessary.

Comparison of the excitation spectrum with the absorption spectrum in solution (Figure 6) shows that the fine structures due to phonon replicas at 540-640 nm for isolated C_{60} are well reproduced in the solid state. This is another manifestation of the molecular character of C_{60} being mostly preserved in the solid state. This is consistent with the explanation of the photoconductivity in terms of Frenkel excitons.

To compare the emission and excitation spectrum, both are plotted on the same photon-energy scale (Figure 7). One notices that each of the

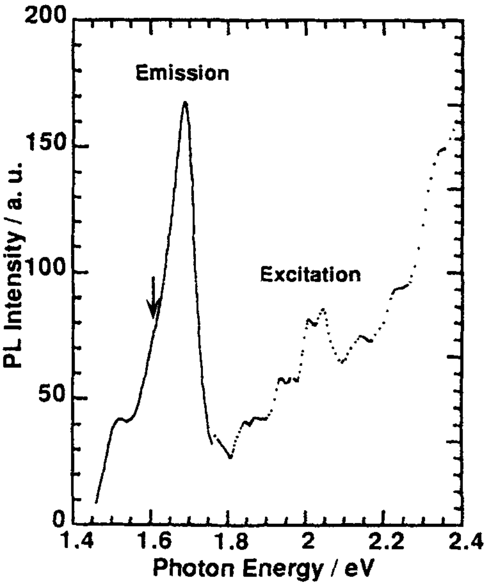

FIGURE 7 Luminescence emission and excitation spectrum at 77K. The arrow indicates a shoulder.

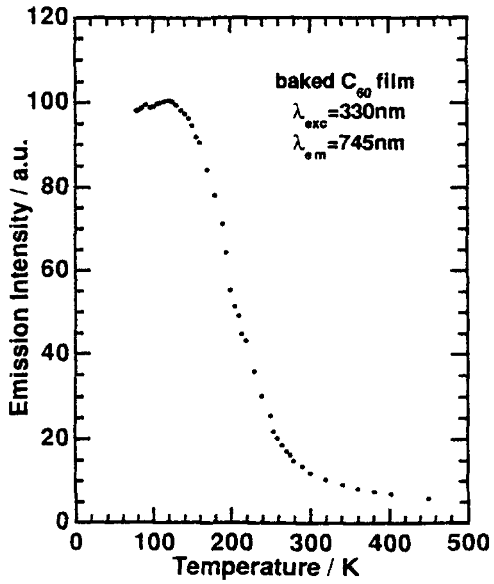

FIGURE 8 Temperature dependence of luminescence intensity.

three main structures in the emission spectrum has a corresponding peak in the excitation spectrum, whose position is symmetrical about $h\nu$ =1.85 eV, probably, the position of a 0-0 transition. This means that the excitation and the emission occur in the same molecular species. Also, we note that the fine structures in the excitation spectrum have quite good correspondence with those in an absorption spectrum at 20K reported by Reber et al.,[6] with the better resolution in the former.

Temperature Dependence of Luminescence

A careful and elaborate measurement was performed to clarify the temperature dependence of luminescence. The results are shown in Figure 8. In this measurement, each data point was taken after steady-state was reached both for the temperature and for the luminescence signal. By this precaution, we are able to discuss the detailed shape of the temperature dependence curve. As demonstrated here, the curve shows a turning point at 250-260K, the well-known phase transition temperature from fcc to sc. The luminescence increased more steeply below this point. This is the first example of a UV/Vis optical property of solid C_{60} affected by the phase transition.

Although the mechanism of this phenomenon should be a subject of further investigations, we would like to suggest two possibilities. The first one is the involvement of intermolecular energy transfer as a quenching process, by which most of excited states eventually reach non-radiative quenching sites. If energy transfer were influenced by molecular arrangement in solid lattice, it would be reasonable to expect the phase transition and temperature change to induce some effect on energy transfer rate, then on luminescence. Another possibility would be that oscillator strength for luminescence has its own dependence on temperature. This can be caused by the forbidden nature of the transition being loosened by local structural distortion induced by the phase transition and/or thermal contraction. If this is the case, not only emission but also absorption due to forbidden transition should change with temperature. A preliminary measurement of absorption spectra as a function of temperature seems to support this expectation.

There are other features in the temperature dependence curve in Figure 8, such as small structures around 200K and a maximum at 120K. They might have some implications for other types of structural change in C_{60} thin film, though more elaborate experiments are necessary to elucidate these matters.

CONCLUSIONS

By the measurements of photoconductivity and luminescence, excited state properties of C_{60} thin film have been studied. The analysis of their temperature dependence gives an insight into the relaxation of optical excitation in solid C_{60} involving both allowed and forbidden transitions. The luminescence excitation spectrum, which has not been reported so far, has revealed new features in the solid-state specific forbidden states around 2.8 eV. The careful measurement of luminescence as a function of temperature has demonstrated the first case of a UV/Vis optical property of solid C_{60} undergoing a clear change due to the phase transition at 250-260K.

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