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In Situ Lateral Photoconductivity of C_{60}/C_{70} Thin Films during and after Vacuum Vapor Deposition

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Lateral photoconductivity was measured during and after vacuum vapor deposition of carbon cluster (C_{60}/C_{70}) thin films. A slight change of slope in a photocurrent increase curve during the thin film deposition suggests the formation of a monomolecular layer of carbon clusters. Photocarrier generation efficiency is found to be higher at an absorption structure around 600 nm.

Since the discovery of a simple preparation technique of carbon clusters such as C_{60} and C_{70},[1] there have been an increasing number of studies on the unusual properties of this new allotropic form of carbon.[2] Particularly noteworthy was the fact that C_{60} can be superconductive when it is doped with alkali metals like potassium and rubidium.[3] In this connection electronic transport phenomena in this new material appear particularly intriguing. Here we report the photoconductivity of undoped carbon cluster thin films measured in situ during and after vacuum vapor deposition.

Refined carbon cluster powder (C_{60}/C_{70} with 5-15% C_{70}) purchased from MER Corporation was used as received. It was placed in an aluminum crucible wound with tungsten wire, and heated to evaporate in a vacuum of $4\text{-}6\times10^{-5}$ Pa. The temperature of the crucible was controlled by a PID temperature regulator (Shimaden FP20). The evaporation process was observed with a quartz oscillation thickness monitor (ULVAC CRTM-7000). Films were deposited at a rate of 1-2 Å/min.

In situ lateral photocurrent was measured using a system shown in a previous publication.[4] A pair of coplanar interdigitated gold electrodes was vacuum-deposited on fused quartz substrates, whose interelectrode gap was

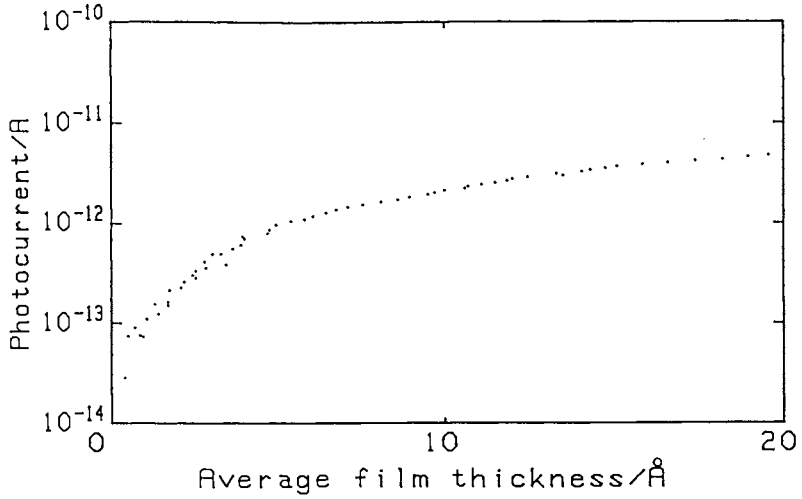

Fig. 1. Increase in lateral photocurrent in carbon cluster thin film during vacuum vapor deposition.

0.1 mm and whose total gap length was 100 mm (10 mm x 10).

A voltage of 1000 V was applied between the gold electrodes creating an electric field of 0.1 MV/cm. The gap area was illuminated with white light from a 150 W Xe lamp filtered by an infrared cut filter. During film deposition, the light was turned on and off periodically with an on-period of 3 s and off-period of 30 s. The light was lead into a vacuum sample chamber using a quartz optical fiber and a light pipe. Lateral photocurrents thus produced were measured with a digital electrometer (Keithley 616).

For the measurement of photocurrent spectra, a monochromator (Nikon G-250) was used together with a neutral density filter servo control system (Optel Corporation). This system kept the number of photons impinging on samples constant irrespective of exciting wavelength, yielding directly photocurrent spectra corrected to a constant photon flux (9×10^{14} $cm^{-2}s^{-1}$).

No photocurrent was to be observed before the vacuum vapor deposition. A few minutes after the start of the deposition, photocurrent of the order of 10^{-14} A appeared and increased. Figure 1 shows the early stage development of lateral photocurrent plotted logarithmically against the average film thickness. After the initial fast rise, the photocurrent increase curve showed a change of slope around a film thickness of 5 Å.

We observed a similar but more pronounced change of slope during the deposition of phthalocyanine (Pc) thin films.[4] Through the scanning electron microscopic observation of very thin Pc films, the change of slope was attributed to the coverage of the entire surface of substrate by very thin Pc layer (thickness:50-60 Å). If we apply the same interpretation to the present

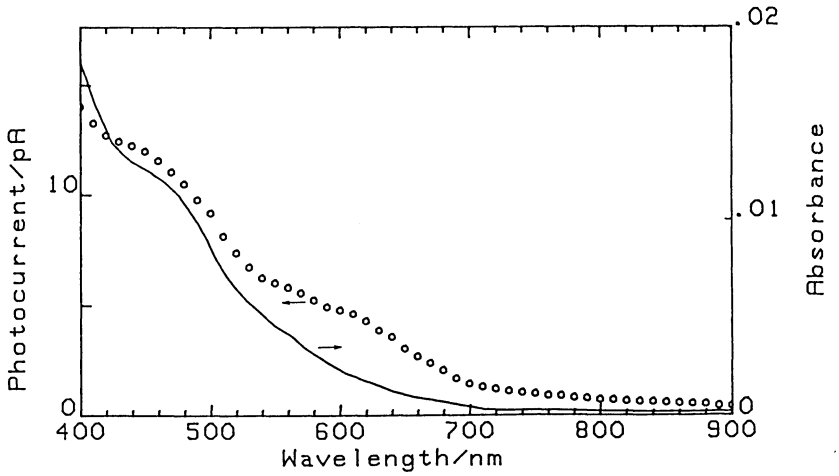

Fig. 2. Photocurrent action spectrum (O) and absorption spectrum (——) of a 40 Å thick carbon cluster film.

results, it is possible that a very thin layer of carbon clusters is formed at a thickness of about 5 Å. Since the diameter of a C_{60} molecule is about 7 Å which is not very different from 5 Å, this may suggest the formation of a monomolecular layer of carbon clusters. Its confirmation, however, should await the electron microscopic observation of carbon cluster films of this thickness.

Figure 2 shows a photocurrent spectrum of a 40 Å thick carbon cluster thin film together with its absorption spectrum. The photocurrent spectrum was measured in a high vacuum without exposing the sample to air. Considering the composition of the deposition source material (C_{60}/C_{70} with 5-15% C_{70}), we expect that the major part of the spectra should be governed by C_{60}. The both spectra agree except for one difference. There are two shoulders at 440-480 nm and at 600-620 nm in the photocurrent spectrum with the latter missing in the absorption spectrum. In a separate absorption measurement, however, a thicker film (thickness:2500 Å) gave a very weak absorption peak around 600 nm agreeing with the result by Kratschmer et al.[1] The absorption shoulder at 450 nm was also observed by Achiba et al. for C_{60} films deposited on alkali halide substrates.[5]

The fact that, in Fig. 2, the 600 nm structure appeared only in the photocurrent spectrum means that the photocarrier generation efficiency is higher around this wavelength. A possible explanation for this is that the small radiative decay rate of the excited states involved leads to the higher chance of electron-hole charge separation. This appears consistent with the suggestion that the optical transition around 600 nm has a forbidden

nature.[6]

The photocurrent was found to vary in proportion to $V^{2.5}$ when the applied voltage (V) was changed from 600 to 1300 V, indicating the involvement of space charge limited currents. The dependence of photocurrent (I_p) on light intensity (L) can be described by the formula, $I_p = kL^n$, where k is a constant. n was found to be 0.51 at 400 nm and 0.58 at 600 nm, when L was changed from $5x10^{14}$ to $5x10^{15}$ $cm^{-2}s^{-1}$. The value of n being close to 0.5 suggests that photocarrier concentration is governed by bimolecular recombination.

The introduction of air to the sample chamber caused a considerable increase in photocurrent as well as in dark current. This indicates a role of oxygen or water as a dopant to carbon clusters. Little change was found in the shape of photocurrent spectra.

The present results demonstrated that carbon cluster thin films have considerable photoconductivity like organic semiconductors such as Pc. The ratio of photoconductivity to dark conductivity, though, appears to be higher than that of Pc. This shows a promise for the photoelectric application of this new material. More detailed study is now in progress.

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