—Communication—

Photovoltage Generation by a Junction of C₆₀ with p-Si

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Received September 7, 1993 ; Accepted November 17, 1993

1. Introduction

The band gap of solid C₆₀ with a face centered cubic (f.c.c) structure was reported to be 1.5 eV by Saito et al¹⁾ using the local density approximation. Following the preparation of C₆₀ thin film, measurements of its optical, photoelectron and inverse-photoelectron spectra were carried out to elucidate its band structure, with subsequent results suggesting that the band gap ranges from 1.5 to 2.3 eV²⁻⁴⁾. In addition, the conductivity of the C₆₀ film was also found to widely vary between 10⁻⁵ to 10⁻¹⁴ S cm⁻¹ (5-7). Although the electrical properties of solid C₆₀ were recently found to be influenced by oxygen intercalation⁸⁾, neither these properties nor the band gap have been well clarified; hence debate remains. The junction of a C₆₀ thin film with a p-type Si single crystal can not be explained theoretically, yet nevertheless a possibility exists for use of C₆₀ in solar energy conversion applications.

2. Experimental

We used substrates of Si single crystals having a conductivity of 0.05 S cm⁻¹. In order to oxidize the Si substrate and provide a thin SiO₂ layer, the substrates were initially dipped for 10 min in a HNO₃ solution at 70 - 80°C. Next they were etched with a HF solution to clean the Si surface. A gold electrode was then immediately evaporated onto the substrate and the oxidation and etching processes were repeated to ensure a clean Si surface prior to C₆₀ vapor deposition. Commercially-available C₆₀ powder (99.9% purity) was evaporated by placing it in a heated tungsten (W) boat and sublimating C₆₀ onto the Si substrate at 500 °C and 10⁻⁵ Torr. The resultant film thickness was about 1.5 μm as determined by scanning electron microscopy (SEM). Finally, an In₂O₃-SnO₂ (95:5) electrode was sputtered on the deposited film. A gold electrode (thin enough to transport the light) was also used for the measurements to confirm that there was no photoelectric effect of the C₆₀/ITO interface. We took I-V measurements from

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Key words: Fullerene, Heterojunction, Solar cell

-15 to 5 V under illuminated and dark conditions. A 150-W Xe lamp (longer than 200 nm in wavelength) was used for photo excitation. The difference of the results with ITO and Au electrodes was not observed. For the conductivity measurements, C₆₀ thin film was deposited on a glass substrate.

3. Results and Discussion

The conductivity of the C₆₀ thin film used in our experiments was measured to be about 10^{-9} S cm⁻¹ which is in the reported range⁵⁻⁷⁾. Figure 1 shows results of our C₆₀/p-type Si junction under dark conditions, where region I indicates values obtained when the samples were positively biased on the Si side causing the main carriers to drift. When the sample was inversely biased (region III), the current produced by the minority carriers was different from that observed for a typical p-n junction, i.e., showing a constant reverse saturation current. The reverse current is believed to be produced by the thermally generated minority carriers existing within a diffusion length on either side of the transition region, which subsequently diffuse into this region and are swept to the other side of the junction by the electric field. Another contributing factor is that minority carriers can be generated in the transition region if it is larger in comparison with the diffusion length. Because the transition region increases with

reverse bias, the reverse current may increase with this bias if the contribution of minority carriers generated in the transition region is significant. C₆₀ layer has only a small number of free electrons originated from the impurities⁸⁾ and after the completion of the diffusion of these free electrons to the p-Si having a large number of holes, the transition region remains deeply in the C₆₀ thin film.; thereby making carrier generation in the transition region an important factor which leads to increasing the reverse current as reverse bias is increased (Fig. 1).

Fig. 1 I-V relation of a junction formed by depositing C₆₀ thin film on a p-type Si substrate measured under dark conditions. In regions I and IV the Si side was positively biased, whereas in II and III the C₆₀ thin film side was positively biased.

Figure 2 shows the resultant voltage behavior of the C₆₀/p-type Si junction in an open circuit under a photo-dark cycle,

where the photovoltage is about 0.2 V. Note the photovoltage decreases to 0 V immediately after the photo illumination is stopped.

Fig. 2 Open circuit voltage response of the C_{60} /p-type Si junction measured under dark and photo-illuminated conditions.

FIG. 3 Enlarged plot of region IV's I-V relation for the C_{60} /p-type Si junction measured under photo-illuminated conditions. The photovoltage is about 0.2 V at zero current.

A detailed plot of the I-V relation for the same junction under photo-illuminated conditions is shown in Fig. 3, and the 0.2-V open circuit voltage is clearly consistent with that obtained under the photo-dark cycle (Fig. 2).

When we use our previous results, in which the the Fermi energy level of C_{60} is 0.58 eV below the conduction band⁹⁾, in conjunction with C_{60} 's electron affinity of 2.6-2.8 eV¹⁰⁾, the Fermi energy level is calculated to be at about 3.4 eV below the vacuum level. Since the Fermi energy level of p-type Si is known to be at about 4.7 eV below the vacuum level, the difference between these levels is about 1.3 eV. Thus, the obtained photovoltage appears to be low, although it can possibly be further enhanced by selecting optimum conditions. In our experiments, it was inevitable to expose samples to the air before measurements, the characteristics obtained would be affected by the oxygen absorption of the C_{60} films. The Fermi energy level of the C_{60} film free from oxygen is expected to be higher than that with oxygen intercalation. It means that a higher photovoltage is expected for a oxygen-free C_{60} sample.

Solid C_{60} has especially attracted intense attention for research of its superconducting properties. Its semiconducting properties,

however, are also of interest because the occurrence of inherent photovoltage generation is expected to lead to much wider applications in many fields. For example, improving the photovoltage via new processes or by changing C₆₀ junction properties through doping treatments make it possible to develop an effective solar cell.

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