Effect of Sublimation Temperature on the Photovoltaic Properties of Amorphous Carbon Thin Films from Fullerene

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Abstract: This paper presents the effects of sublimation temperature of C_{60} fullerene on the photovoltaic properties of amorphous carbon (a-C) films synthesized by remote plasma cracking. Here, we show that the deposition rate increases rapidly,Raman peak intensity corresponding to disordered fullerene becomes strong and the optical band gap increases with increasing the sublimation temperature. The photovoltaic devices with structure of Al/C_{60}/a-C/ITO glass are fabricated with different sublimation temperatures and therelationship between the photovoltaic properties and the material properties of a-C films are discussed. It is shown that the improvementof power conversion efficiency is explained by low component of disorderedC_{60}in amorphous carbon at lower sublimation temperature.

Keywords: Carbon, photovoltaic, amorphous, fullerene, sublimation.

1. INTRODUCTION

Si has been studied as solar cell material for more than six decades since the photovoltaic effect of Si was discovered in 1950's. Now solar energy derived from Si solar cells has attracted attention as a next generation energy source instead of fossil fuels [1, 2]. However, the production cost of Si solar cell is high because high purity Si is necessary for high efficiency solar cell. In order to reduce the cost of solar cell, several kinds of inorganic materials have been studied, such as copper indium selenide (CIS), GaAs, CdTe, Cu_2O, etc. Moreover, dye-sensitized solar cell [3], organic solar cell [4] and perovskite solar cell [5] have been emerged as next generation solar cell recently. But there is problem in long-term stability, efficiency, etc for the spread of photovoltaics.

Carbon-based photovoltaic solar cells have attracted interest as next generation solar cell because of the various outstanding properties of carbon. Fullerene [6], carbon nanotube (CNT) [7], graphene [8] and amorphous carbon (a-C) [9] have been studied as a solar cell material because of the unique properties of nano carbons until now. The homojunction carbon solar cell was first reported by Sharon *et al.* in 1997 [10-12]. Then, the solar cells with the structures of C_{60}/Si [13], CNT/Si [14], graphene/Si [15] and a-C/Si [16] etc. have been reported. Among various kinds of carbon material, a-C has attracted because the large area deposition is easy,and it is possible to tune the band gap with changing the growth conditions. a-C/Si heterojunction have been studied with both n-C/p-Si type [17] and p-C/n-Si type [18] byusing plasma chemical vapor deposition (CVD) [19], ion beam sputtering [20], thermal CVD [21], etc.. More recently, the concept of all-carbon solar cell has been proposed [22], and thin-film-based all-carbon photovoltaic device [23] and a-C-based bulk-heterojunction solar cell [24] have been proposed. However, the structural control of a-C and impurity doping are still difficult for high power conversion efficiency.

The authors have reported all-carbon photovoltaic devices using a-C as a p-type layer and C_{60} as an n-type layer for the first time in 2013 [23], where a-C thin films were synthesized by remote plasma cracking, where N_2 radicals were exposed to C_{60} in vacuum during the sublimation.The a-C film and the C_{60} film show p-type and n-type weakly, respectively [23]. But the power conversion efficiency is too low for practical application. In order to improve the power conversion efficiency, understanding the effects of structures and properties of amorphous carbon on the photovoltaic properties is necessary. It is believed that the control of the deposition parameter which affects the optical and electrical properties of amorphous carbon films is a key issue for the efficiency improvement. Although the effect of sublimation temperature on the properties of amorphous carbon filmsis very important, there is no report on that. This paper presents the effects of sublimation temperature on the structural and optical properties of amorphous carbon thin films. Then the amorphous carbon-based photovoltaic devices are fabricated with changing the sublimation temperature and the photovoltaic properties are discussed.

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2. EXPERIMENTAL

Amorphous carbon thin films were deposited on glass substrate by exposing N_2 radical to sublimated C_{60} (99.5%) in the ultrahigh vacuum chamber with the base pressure of 10^{-8}torr. The deposition system consists of C_{60} Knudsen cell, N_2 radical cell, turbo-molecular pump (TMP), load-lock chamber, etc. The schematic view of the ultra-high vacuum system is illustrated in Figure **1**. There is no intentional substrate heating during the deposition. The rf power, the rf frequency and N_2 flow rate are300W, 13.56 MHz and 1.5 sccm, respectively. The pressure during the deposition is 1.1 – 1.3 x 10^{-4}torr. The sublimation temperature of C_{60} was varied from 450 to 500 °C. The deposition duration is two hours unless otherwise mentioned. The samples were characterized by Raman scattering using the laser with the wavelength of 532 nm, UV-Vis spectrophotometer, atomic force microscopy (AFM), etc.

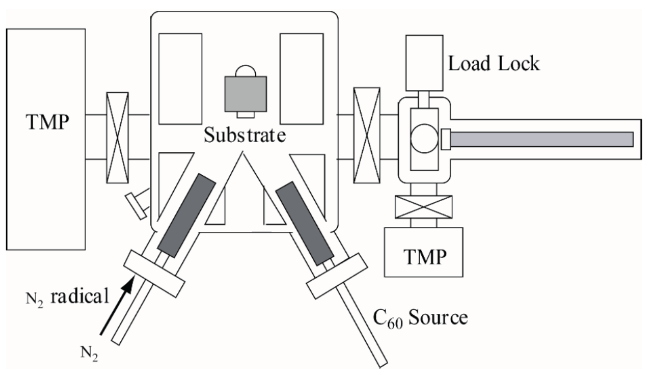

Figure 1: Schematic illustration of ultra-high vacuum system for the deposition of a-C and C_{60} films.

In order to evaluate the properties of a-C for photovoltaic device, a-C film and C_{60} film were deposited on ITO (indium tin oxide) -coated glass sequentially. For the deposition of C_{60} film, the N_2 radical was switched off. After formingAl electrodeby vacuum evaporation, the current-voltage (I-V) characteristics were measured under the standard light of AM 1.5 illumination. Photovoltaic parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and PCE (power conversion efficiency) were measured from the I-V curves. FF was calculated by the ratio of solar cell maximum electric power to open circuit voltage multiplied by short circuit current. PCE was calculated by the ratio of solar cell maximum electric power to incident optical power. The active area of device is 9mm^2. The thickness of a-C and C_{60} were kept constant to 100nm and 50nm, respectively. The structure of photovoltaic device is almost the same as reported in ref. 23.

3. RESULTS AND DISCUSSIONS

3.1. Properties of Amorphous Carbon Films

The deposition rate of amorphous carbon films for different sublimation temperature from 450 to 500 °C is shown in Figure **2**. The deposition rate increases rapidly with increasing the temperature. This is due to the high evaporation rate of C_{60} at higher sublimation temperature. The super linear increase of C_{60} film evaporationrate in the case of vacuum evaporation is reported by Drozdov el al [25], which is consistent with our results.

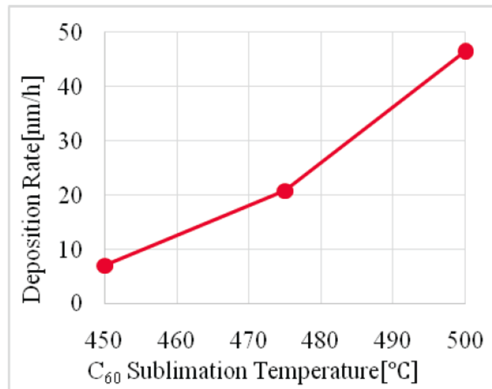

Figure 2: Deposition rate of a-C films for different sublimation temperatures (450 °C, 475°C and 500 °C).

Raman spectra of amorphous carbon films deposited at various temperatures from 450 to 500 °C are shown in Figure **3**. The spectra are well fitted by three peaks of D-peak at around 1380 cm^{-1}, G-peak at around 1574 cm^{-1} and disordered C_{60} peak at around 1460 cm^{-1}[23] as indicated by the dotted line. D-peak is from disordered graphitic carbon phase[26] and G-peak is from graphitic carbon phase [27], which is usually observed in amorphous carbon films. The peak position of these peaks does not change very much at different temperatures. However, it is interesting to note that the disordered C_{60} peak becomes stronger and D-peak becomes weaker with increasing the sublimation temperature. It means that the component of disordered C_{60} exists in a-C films, and the increase of disordered C_{60}component with increasing the sublimation temperature is due to the difficulty in decomposing C_{60} in the plasma because of the high deposition rate at high sublimation temperature (Figure **2**).

Figure **4** shows the optical band gap of amorphous carbon films at different sublimation temperatures derived from by Tauc plot from transmission spectra and reflectance spectra assuming indirect transition.

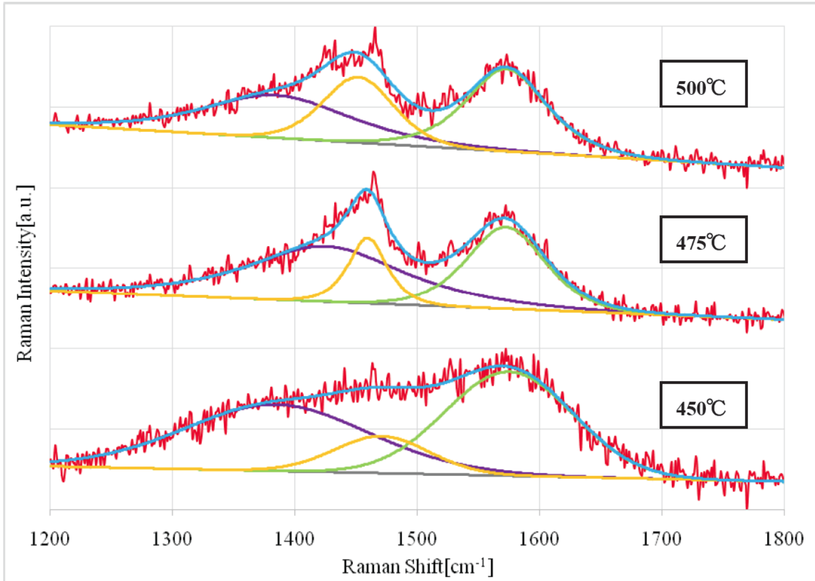

Figure 3: Raman spectra of a-C films for different sublimation temperatures (450 °C, 475 °C and 500 °C).

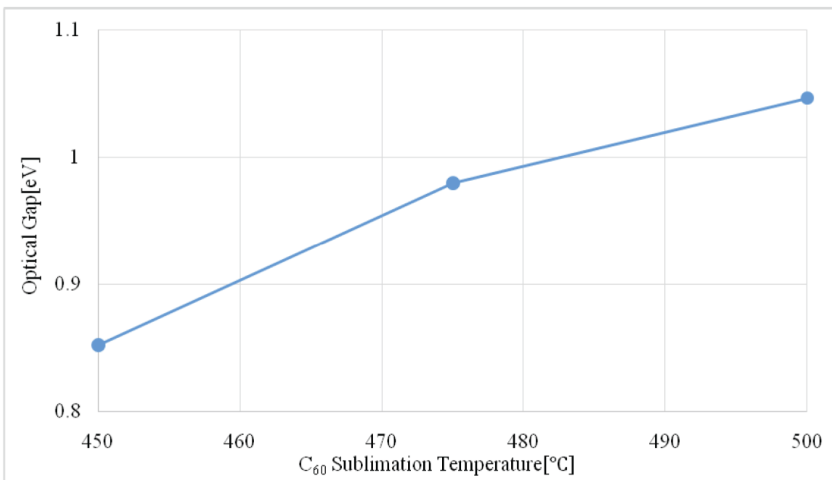

Figure 4: Optical band gap of a-C films for different sublimation temperatures (450 °C, 475 °C and 500 °C).

The optical band gap increases gradually with increasing the sublimation temperature. The increase of optical band gap is due to the decrease of sp^2 cluster size at high sublimation temperature, resulting from the increase of percentage of C_{60} in amorphous carbon film. The similar results havebeen reported in boron-doped amorphous carbon films by rf plasma CVD [13].

Figure **5** shows the AFM images of carbon films deposited at various sublimation temperatures. The surface is smooth (rms value is around 1 nm) and the structure is not observed in all the samples. It means that the effect of surface morphology on the photovoltaic properties is negligible when the sublimation temperature is varied.

3.2. Photovoltaic Properties

The photovoltaic properties of amorphous carbon-based photovoltaic devices deposited at 450 °C and 500 °C were tested. The structure of the device is Al/C_{60}/a-C/ITO glass as mentioned before. The I-V characteristics of two devices under AM 1.5 illumination are shown in Figure **6**. The open circuit voltage, short circuit current density, fill factor and power conversion efficiency are summarized in Table **1**. There is no significant difference in open circuit voltage and fill factor by changing the temperature. However, the short circuit of the device with the sublimation temperature of 450 °C is about three times higher than that of 500 °C. This is explained as follows. The photo-generated carriers in n-type C_{60} film and p-type a-C film are collected as current as reported in ref. 23. As shown in

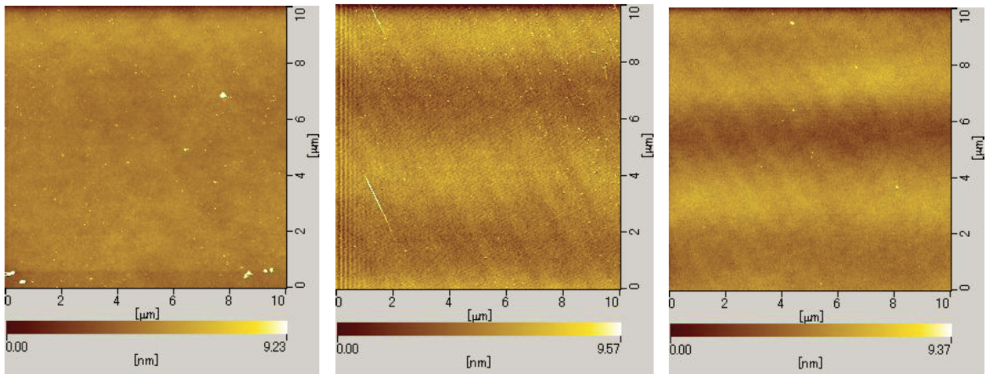

Figure 5: AFM images of a-C films for different sublimation temperatures (450 °C, 475 °C and 500 °C).

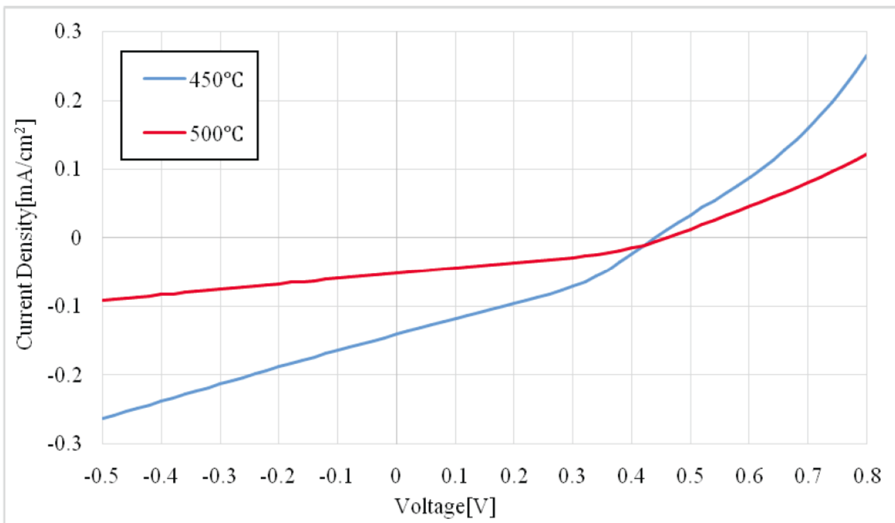

Figure 6: Current density-voltage characteristics of a-C/C_{60} photovoltaic devices under AM 1.5 illumination condition fabricated at different sublimation temperatures (450 °Cand 500 °C).

Figure **3**, the component of a-C is a mixture of disordered graphitic carbon and disordered C_{60}. When the sublimation temperature is increased to 500 °C, the percentage of disordered C_{60}in a-C layer is increased with high deposition rate. If the percentage of disordered C_{60} becomes high in a-C layer, the recombination of photo generated carriers in the amorphous carbon is increased because of the high density of defects due to disordered C_{60}, resulting in the small short circuit current.

Figure **7** shows the energy level alignment of this device estimated from the literatures. From this figure the photo voltage of around0.6 V is expected, but our result shows that the open circuit voltage is less than 0.5 V. This degradation will be due to the high density of defects in a-C and C_{60} films. There is no large difference in the open circuit voltage for different sublimation temperature because it is determined by the HOMO and LUMO levels of a-C and C_{60}. In order to minimize the deposition time, 500 °C is better, however, for the improvement of power conversion

Table 1: Photovoltaic Properties of Al/C_{60}/a-C/ITO Glass for Different Sublimation Temperature

Sublimation temperature [˚C]	Open circuit voltage *V*oc[V]	Short circuit current density *J*sc[mA/cm^2]	Fill factor FF	Power conversion efficiency *η*[%]
450˚C	0.44	0.14	0.35	0.021
500˚C	0.46	0.052	0.36	0.0085

efficiency, lower sublimation temperature (450 °C) is preferred.

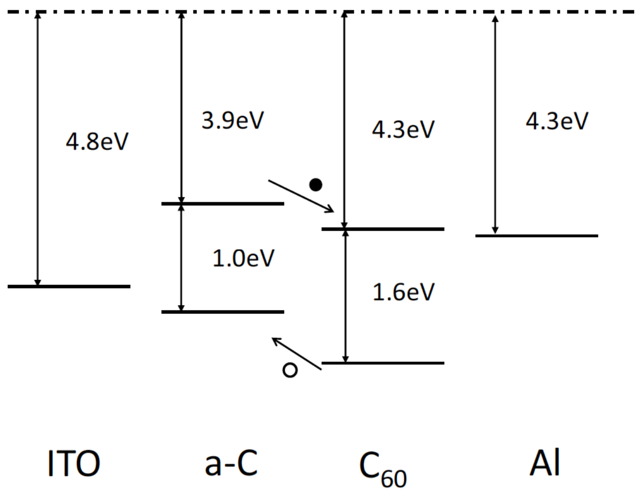

Figure 7: Energy level alignment of ITO/a-C/C_{60}/Al device estimated from the literatures.

4. CONCLUSION

Amorphous carbon films were synthesized by remote plasma cracking of C_{60} with varying the sublimation temperature. The deposition rate was increased, the percentage of disordered C_{60} in a-C increased and the optical band gap increased with increasing the sublimation temperature. The structure of Al/C_{60}/a-C/ITO glass showed photovoltaic properties. The power conversion efficiency was higher when the lower sublimation temperature was employed for a-C deposition.The improvement is due to the reduction of the component of disordered C_{60} in a-C layer at low sublimation temperature.

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