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结晶性和粒子尺寸对 C_{60} 薄膜晶体管迁移率的影响

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摘要：采用真空沉积方法在不同基片温度(30~190 ℃)和沉积压力(1×10^{-4} 和 1×10^{-1} Pa)下制得了 C_{60} 薄膜。研究了薄膜的结晶性和晶粒尺寸对迁移率的影响。采用 X 射线衍射和原子力显微镜表征了薄膜的结构和形貌,发现提高基片温度,薄膜的结晶性和晶粒尺寸均提高;提高沉积压力,薄膜的晶粒尺寸增大而结晶性不变。场效应测试结果表明,C_{60} 薄膜的迁移率与其结晶性密切相关,高的结晶性有利于获得高迁移率;不同于平面有机半导体材料,对于球状 C_{60} 半导体材料,大的晶粒尺寸可能导致低迁移率。

关键词：富勒烯；薄膜晶体管；迁移率；结晶性；晶粒尺寸
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Effect of Crystallinity and Grain Size of Film on Mobility of C_{60} Thin Film Transistors

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Abstract: Fullerene (C_{60}) thin films have been prepared on SiO_2 substrates by vacuum deposition under different substrate temperature ranging from 30 to 190 ℃ and deposition pressure of 1×10^{-4} and 1×10^{-1} Pa. The effect of crystallinity and grain size on the mobility of the deposited C_{60} thin films are investigated. X-ray diffraction and atomic force microscopy observation indicates that both the crystallinity and the grain size of the C_{60} films increase with increasing substrate temperature. And the grain size of the films increase and the crystallinity keep almost unchanged with increasing deposition pressure. Field-effect measurements indicate that the mobilities of the C_{60} thin films are closely correlated with their crystallinities, and the increased crystallinity of the films gives the improved mobility. Different from the films of planar organic semiconducrors molecules, for the spherical C_{60} molecules films, the larger grain size could lead to the lower mobility.

Keywords: fullerene; thin film transistors; mobility; crystallinity; grain size

0 Introduction

In recent decades, organic thin film transistors (OTFTs) have received considerable attention owing to their low cost, low temperature process, compatibility with plastic substrate, and wide potential applications in large-area, lightweight, flexible electronics devices such as electronic displays, organic memories, and sensors[1-5]. Much research work has been focused on obtaining high performance OTFTs comparable to those of amorphous silicon thin film transistors (TFTs)[6-10]. In addition to the optimization of device structure and performance, the correlation of the charge transport with the thin-film microstructure has also been extensively studied. It is well known that the charge transfer in OTFTs highly rely on the crystallinity,

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molecular ordering and crystal grain sizes, which in turn depend on the molecular structures of the organic semiconductors[11-12], deposition process[13-16], and substrates[17-18]. For the most planar organic semiconducrors molecules, such as CuPc, F_{16}CuPc, pentacene, perylene bisimide and oligothiophene, increasing substrate temperature (T_s), decreasing deposition rate, and incre-asing deposition pressure in vacuum deposition process normally leads to a highly ordered film with larger grain sizes and fewer grain boundaries, which is regarded as the most effective way to obtain high-mobility devices[14-25]. However, for the spherical C_{60} semiconductor, which is an important n-type semiconductor material with high mobility, the mechanism of charge transport in C_{60} films is still unclear, and the relationship between mobility and microstructure of the C_{60} films is controversial[20,26-28]. Therefore, it is essential to investigate the effect of morphology and structure, which are quite sensitive to growth conditions, on the performance of the C_{60} films in-depth. In this study, the crystallinity and grain size of the C_{60} films have been regulated by changing the T_s and deposition pressure in the vacuum deposition process. X-ray diffraction (XRD) and atomic force microscopy (AFM) were used to investigate the morphology and crystalline structure of thin films. Furthermore, the mobilities of the films are obtained by field-effect measurements, and the correlations of mobility with crystallinity and grain size of the C_{60} films are established.

1 Experimental

1.1 Fabrication of C_{60} TFTs

Fig.1 shows the schematic diagram of the fabricated C_{60} TFTs. C_{60} (99.9%) is purchased from Aldrich and used without further purification. The substrate is 300 nm SiO_2 thermally grown on a heavily doped n-Si wafer, which were ultrasonically cleaned with acetone, isopropyl alcohol, and ultrapurified water, successively. A bottom-gate, top-contact device configuration of C_{60} TFTs was adopted. First, the substrate was set in the chamber and maintained at 4×10^{-5} Pa. Subsequently, a 40 nm thick C_{60} active layer[16], patterned through a shadow mask, was deposited by vacuum evaporation onto the substrate under a specific T_s (*i.e.*, 30, 60, 90, 130, 160 and 190 ℃) at the same rate of 0.01 nm·s^{-1} recorded by a quartz crystal oscillator. Finally, the gold (Au, 99.99%) electrodes, with a thickness of 50 nm, were defined on the C_{60} film by thermal evaporation through another mask. For the samples of different deposition pressure, the films were deposited by vacuum deposition under a specific P_{dep} (*i.e.* 1×10^{-4} and 1×10^{-1} Pa) with the rate of 0.01 nm·s^{-1} and the T_s of 130 ℃.The channel length (L) and width (W) are 70 and 500 μm, respectively.

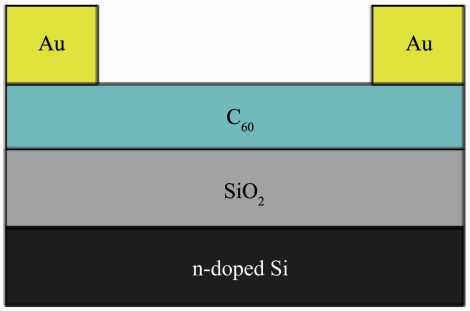

Fig.1 Schematic diagram of the fabricated C_{60} TFTs

1.2 Charcterization

The structures and surface morphologies of the films were characterized by X-ray diffraction (XRD, Philips X′pert Pro X-ray diffractometer in 2θ range of 15°~28°, Cu $K\alpha_1$ radiation of 0.154 nm) and atomic force microscopy (AFM, Bruker Dimension Icon, tapping Mode). The performances of the devices were evaluated by semiconductor characterization system (Keithley model 4200-SCS) under vacuum condition at room temperature.

2 Results and discussion

2.1 Surface morphology and structure of C_{60} films

The characteristic XRD patterns and morphologies of the C_{60} films deposited under different T_s are shown in Fig.2. The XRD patterns of the C_{60} films show broadened (113) peaks, corresponding to the D values of *ca.* 1.54 nm. With increasing T_s from 30 to 190 ℃, the intensity of (113) peaks increase, indicating the increased crystallinity of the films (Fig.2A). The

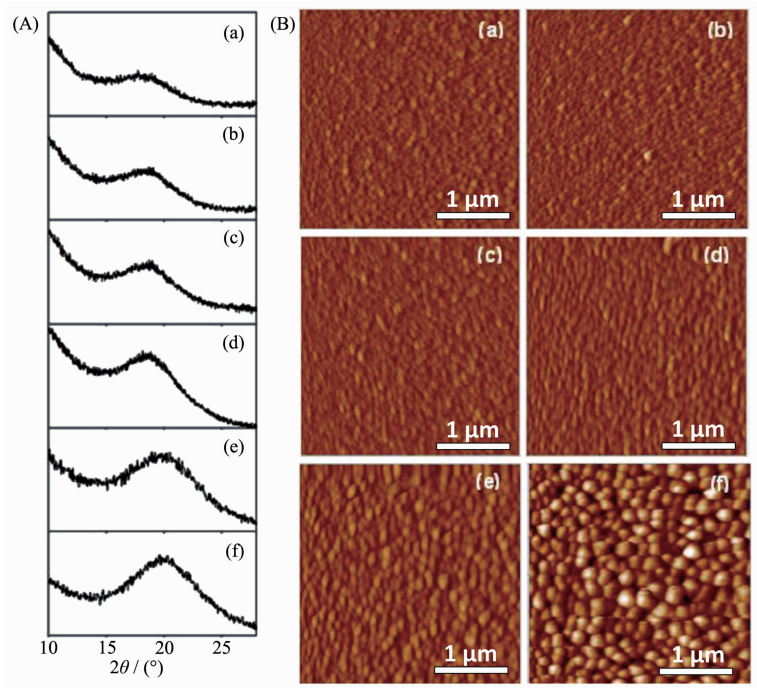

Fig.2　Characteristic XRD patterns (A) and AFM images (B) of the 40 nm C_{60} films deposited under different T_s of 30, 60, 90, 130, 160 and 190 ℃ (a~f), respectively

morphological evolutions of the C_{60} films with T_s are demonstrated in Fig.2B. It is clearly seen, the grain sizes keep almost unchanged for T_s below 90 ℃(Fig. 2B(a~c)), and gradually increase for further increasing T_s from 90 to 190 ℃ (Fig.2B(d~f)). The root-mean-square roughness of all the samples obtained from the AFM measurements are about 1~3 nm, indicating the smooth surfaces of the films.

2.2　Electronic properties of C_{60} films

Fig.3 shows the output characteristics of C_{60} TFTs prepared under different T_s. The C_{60} TFTs exhibit typical n-channel field-effect behavior, operated under a positive voltage source-drain voltage (V_d) and gate voltage (V_g), with distinct linear and saturation regions in the output curves. With increasing T_s from 30 to 130 ℃, a significant increase of saturation drain current (I_d) from 1.8 to 12.3 μA is observed when they are biased at V_d=60 V and V_g=60 V (Fig.3a~d). With further increasing T_s to 160 and 190 ℃, I_d decreases to 4.2 μA and 2.1 μA, respectively.

Fig.4 shows the transfer characteristics of C_{60} TFTs prepared under different T_s. From the transfer curves, the carrier mobility are extracted for each device, and the relationship between the mobilities and T_s are shown in Fig.6. In order to make clear of the correlation of the mobilities with the corresponding crystallinity and morphologies of the C_{60} films, the changes of (113) peak intensity and grain sizes with T_s are re-plotted here. It is seen that, for C_{60} films with T_s below 130 ℃, the mobilities increase from 0.026 to 0.211 $cm^2 \cdot V^{-1} \cdot s^{-1}$ with increasing T_s. With further increasing T_s to 160 and 190 ℃, mobilities decrease to 0.082 and 0.030 $cm^2 \cdot V^{-1} \cdot s^{-1}$, respectively. Because of the unchanged grain sizes of C_{60} films deposited

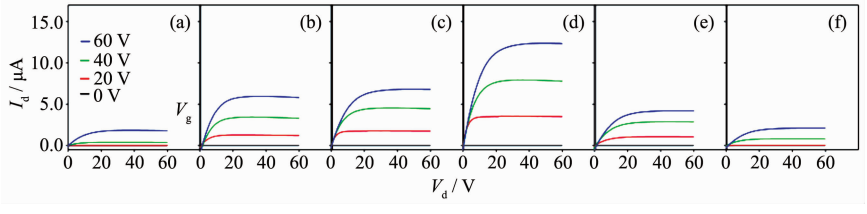

Fig.3　Output (I_d-V_d) characteristics of C_{60} TFTs prepared under different T_s of 30, 60, 90, 130, 160 and 190 ℃ (a~f)

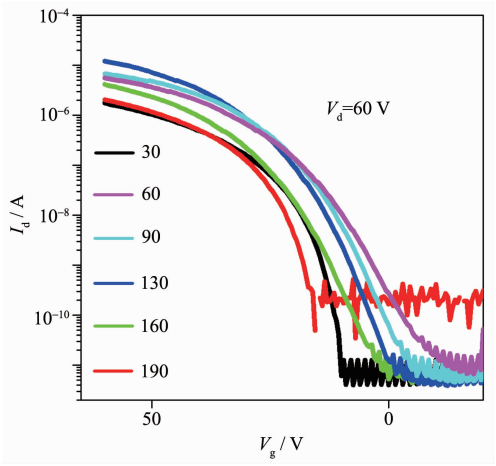

Fig.4 Transfer (I_d-V_g) characteristics of C_{60} TFTs prepared under different T_s of 30, 60, 90, 130, 160 and 190 ℃

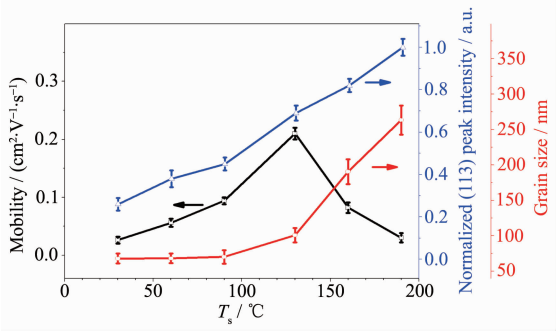

Fig.5 Carrier mobilities, grain sizes, and crystallinity ((113) peak intensity) of C_{60} thin films as functions of T_s

under 30, 60 and 90 ℃, the increase of mobilities could be attributed to the increased crystallinities of films. When T_s is up to 130 ℃, the larger mobility was achieved mainly due to the higher crystallinities despite the slightly increased grain sizes. Interestingly, for the films with T_s of 160 and 190 ℃, despite the increases in the crystallinities, remarkable decreased mobilities are obtained, which should be related the obviously increased grain sizes. These results suggest the different grain-boundary effect for the spherical C_{60} molecules from that for the planar molecules, such as CuPc, pentacene, TIPS-pentacene, perylene bisimide and oligothiophene[14-25]. For the planar molecules, the grain boundary is a crucial barrier for the carrier transport, since the intermolecular charge hopping across the grain boundaries is less efficient than that within the grains. Thus, reducing the grain boundaries by increasing grain sizes is a promising approach to improve charge transport and mobility. However, for the C_{60} samples with T_s of 160 and 190 ℃, the larger grain sizes of spherical C_{60} films lead to the lower mobilitis, which is interesting and worth further investigating.

In order to reveal the influence of grain sizes on the mobilities of C_{60} films, the samples with similar crystallinities and different grain sizes are needed. In our previous study, we have demonstrated that higher deposition pressure in vacuum deposition could lead to the larger grain sizes of C_{60} films with unchanged crystallinities and molecular packing[16]. Thus, the C_{60} films with deposition pressure of 1×10^{-1} Pa and T_s of 130 ℃ are deposited and investigated. In contrast to the C_{60} films with deposition pressure of 1×10^{-4} Pa (Fig.2Ad and 2Bd), the samples of 1×10^{-1} Pa show the unchanged crystallinities and increased grain sizes, as shown in Fig.6. The C_{60} films with deposition pressure of 1×10^{-1} Pa have a mobility of 0.030 $cm^2 \cdot V^{-1} \cdot s^{-1}$, which is lower than the value of samples with deposition pressure of 1×10^{-4} Pa. Due to the unchanged crystallinities, the decrease of mobility should be corrected to the increased grain size.

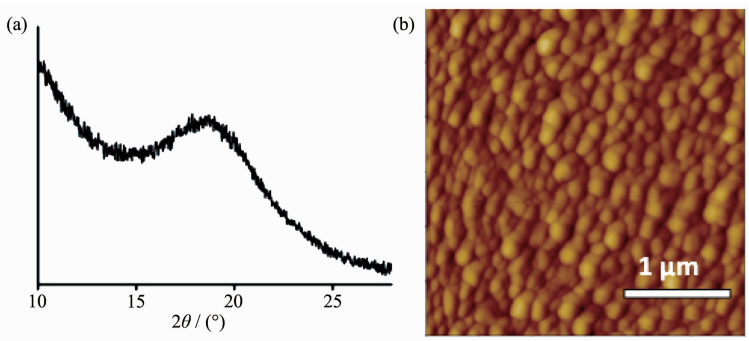

Fig.6 Characteristic XRD pattern (a) and AFM image (b) of the 40 nm C_{60} films deposited under 1×10^{-1} Pa and 130 ℃

As known, the performance of OTFTs is determined by the crystalline order and grain sizes of the first few molecular layers of the semiconductor near the semiconductor/dielectric interface. To ascertain the grain sizes of the C_{60} layers at C_{60}/SiO_2 interface, two C_{60} films of 10 nm thickness were deposited on SiO_2 at deposition pressure of 1×10^{-4} and 1×10^{-1} Pa, respectively. From the corresponding AFM images in Fig.7a and b, it is seen that, the 10 nm C_{60} films deposited under 1×10^{-4} Pa have a lot of small grains, while some larger grains are observed for the films of 1×10^{-1} Pa. This confirmed that larger grain sizes of C_{60} films result in the lower mobilities. The possible mechanism for the effect of grain size on mobility of C_{60} films is proposed in Fig.7c and d. For the spherical C_{60} molecules, carrier could be effectively transported through nearest-neighbor hopping between molecules[26]. So the films with small and close grains are advantageous to effective charge transport (Fig.7c). For the films with large grain size, it is difficult to realize the nearest-neighbor hopping between grains molecules, due to the large spacing between the grains (Fig.7d). Thus, the grain boundary is not a serious barrier for the charge transport, and the larger grain size could lead to the lower mobility in C_{60} TFTs.

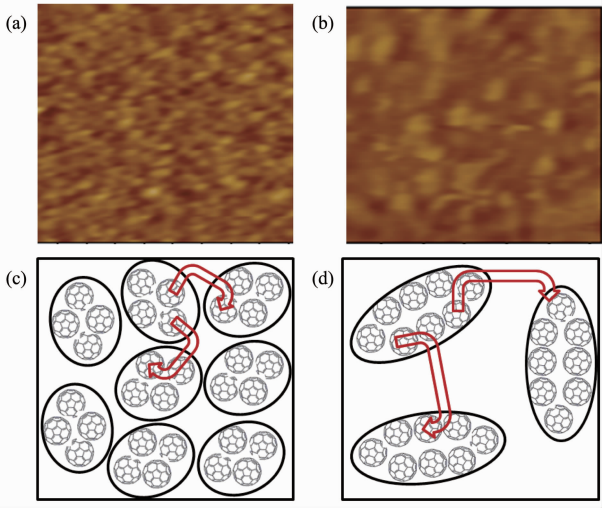

Fig.7　AFM images of 10 nm C_{60} films deposited under (a) 1×10^{-4} and (b) 1×10^{-1} Pa, and the possible charge transfer mechanism of C_{60} films with different grain size (c, d)

3　Conclusions

In summary, C_{60} films have been prepared on SiO_2 substrates by vacuum deposition under different substrate temperature ranging from ranging from 30 to 190 ℃ and deposition pressure of 1×10^{-4} and 1×10^{-1} Pa. The experimental results indicate that the crystallinity and grain size of the C_{60} films thereof the mobility of the obtained TFTs could be effectively regulated by tuning substrate temperature and deposition pressure. A clear correlation of mobility with crystallinity and grain size of the C_{60} film is established. It is found that, both the crystallinity and the grain size of the C_{60} films increase with increasing substrate temperature. And the grain sizes of the films increase and the crystallinity keep almost unchanged with increasing deposition pressure. The mobilities of the C_{60} films are closely correlated with the crystallinity and grain size. The increased crystallinity of the C_{60} films gives the improved mobility. Different from the films of planar organic semiconducrors molecules, for the spherical C_{60} molecules films, the larger grain size could lead to the lower mobility. This study is helpful for the understanding of the charge transfer process and improving the performance of OTFTs.

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