Preparation of Fullerene Polycrystalline Films on Different Substrates by Physical Vapor Deposition

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Fullerene (C₆₀) films were prepared on Si, ITO, and Cu substrates by the physical vapor deposition (PVD) method. It was observed that the morphology and structure of fullerene films strongly depend on the substrates. Along with the interactions between fullerenes and substrates increasing from ITO, Si to Cu substrate, C₆₀ forms small polycrystalline grains, large polycrystalline grains and fullerene oligomers under the same experimental conditions. The irreversible C₆₀ polymerization on Cu substrate is suggested to be catalyzed by the copper metal.
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1. Introduction

Over the last ten years, the study of fullerene films has attracted extensively interests¹⁻³ due to their promising applications in various fields such as nanodevices,^{4,5} optics,⁶⁻⁸ electrochemistry^{9,10} etc. Dozens of methods,^{9,11-17} e.g., electrophoretic depositions,⁹ solvent evaporation,^{11,12} physical vapor deposition,^{13,14} molecular-beam epitaxy,¹⁵ layer-by-layer assembly,¹⁶ and Langmuir-Blodgett films¹⁷ etc., were developed to prepare the fullerene films, and the morphology and structure of these as-prepared films were characterized by STM, AFM, LEEDS, XRD, XPS and various other spectroscopic techniques.

Fullerene films are generally either in polycrystalline form or in fullerene cluster form, depending on the film preparation method. Especially, the choice of substrates plays a crucial role, for example, C₆₀ epitaxial films are prepared with perfect layered substrates in the ultra-high vacuum conditions,¹⁸ and polycrystalline films are prepared on high-quality semiconductor or passivated surfactant-mediated substrates.^{13,14} In fact, it is the fullerene-substrate interaction that determines the morphology and structures of fullerene films.

Since the interactions between C₆₀ and most typical substrates have been studied by the STM technique, the substrates for fullerene deposition can be roughly classified as three catalogues based on the fullerene/substrate interactions, i.e., metals, metal oxides, and semiconductors. Among them, metal oxide substrates usually have the weakest fullerene-substrate interactions as they lack dangling bonds on the surface; semiconductor substrates such as Si(111) ranked the second for having a large number of dangling bonds on the surface. In this case, the mobility of C₆₀ is largely reduced, though the C₆₀-substrate interaction is still van der Waals' bonds and there are no charge transfers between the fullerenes and substrates.^{19,20} Finally, metal substrates such as Cu plates have the strongest fullerene/substrate interactions due to the essential electron transfers

between C₆₀ and some sites of the substrate.²¹

In this letter, we selected three typical substrates, i.e., the silicon, indium tin oxide (ITO) and copper, representing the semiconductor, the metal oxide, and the metal substrates to study the C₆₀ film formation process. The results revealed that the fullerene-substrate interactions indeed affect the morphology and crystalline structure of C₆₀ films.

2. Experimental Details

Figure 1 schematically depicts the PVD setup used in this study. The main compositions of the setup are a quartz tube that connects to a high-vacuum system, and a temperature-controlled furnace. In a typical synthesis, 20 mg C₆₀ powders sample with 99.5% purity was put inside the quartz tube for sublimation. Three plates, i.e., Si [Si(111) single crystal, General Research Institute for Nonferrous Metals], Cu [Cu polycrystalline plate, Beijing Tongxian Chemical Co.], and ITO (Southern China Glass Scientific Co., Beijing), were selected as substrates. The Si slices and ITO were washed with detergent, distilled water, alcohol, and acetone in turns. The Cu substrate surfaces were prepared by electrochemical polishing. The surfaces roughness of Si, Cu and ITO substrates were characterized by SEM and AFM. It was revealed that the surfaces of either Si(111), Cu, or ITO substrates are flat in nm scale. After chemical cleaning, the

Fig. 1 Schematic diagram of the PVD setup. (1). Quartz tube connecting to vacuum system. (2). Deposition substrate holder and 3 substrates on the holder, in which substrate 1, 2, and 3 are Si(111), Cu, and ITO plates separately. (3). C₆₀ powder. (4). Temperature-controlled furnace.

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Fig. 2 SEM and XRD spectrometry study of the C_{60} deposition on Si(111) surfaces. (a), (b) and (c). SEM images of C_{60} film at different scales. (d). XRD pattern correspond to C_{60} film on Si surface.

substrates were put inside the quartz tube near the C_{60} source (ca. 5 cm). As shown in the insert of Fig. 1, the three substrates were set parallel along the tube axial direction to maintain identical environments. Before experiments, both C_{60} and the substrates were first degassed in vacuum system (10^{-3} Pa) for several hours, and then heated up the C_{60} with a temperature-controlled furnace (Tianjin Zhonghuan Co., China) for sublimation. The C_{60} sublimation temperature was set at 550°C , and the substrates' temperature was measured between 350°C and 370°C .

After 10 min. deposition of the C_{60} sample, the substrates showed black color, and the samples were analyzed by scanning electronic microscopy (SEM, Hitachi S-4300F) and XRD (Rigaku Dmax/rb diffractometer with $\text{CuK}\alpha$ radiation, $\lambda = 0.1542\text{ nm}$, 40 kV, 100 mA) to characterize their morphology and structures.

3. Results and Discussions

Low C_{60} coverage on Si(111) was recently studied by Stimpel *et al.*²⁰⁾ with STM technique. It was revealed that C_{60} molecules interact directly with the high density of dangling bonds on the Si(111) surface and lead to low C_{60} surface mobility, so fullerenes distribute disorderly in the first layer. After the Si(111) surface was passivated efficiently with the first layer of C_{60} , the C_{60} surface mobility increases and ordered C_{60} crystalline structures are formed from the second layer. However, since the stress of first layer of C_{60} molecules acts on the upper C_{60} layers and prohibits long-range ordered C_{60} crystalline growth, many small islands of the ordered C_{60} crystalline structure were observed on the second C_{60} layers. Following the subsequent PVD process, these C_{60} islands grow along some preferential facets and forms many polycrystalline grains, as shown in Fig. 2.

In Fig. 2(a)–(c) the SEM images show clearly the regular polycrystalline pattern of the C_{60} film. The typical size of each C_{60} crystalline grain is ca. $0.5\text{ }\mu\text{m}$. XRD is employed to determine the preferential growth orientation of the C_{60} polycrystalline grains, and as shown in Fig. 3(d), the three main peaks in the XRD spectrum correspond to C_{60} (111), (220) and (311) planes. Because C_{60} single crystal exhibits only two types of morphological facets,^{22,23)} i.e., (111) and (200), the strong peaks of some high index facets (220) and (311) reveal the formation of C_{60} polycrystalline grains. The SEM and XRD results are consistent with each other. According to experimental process and XRD data analyses, the thickness of the film is about 100 nm.

ITO is a typical electrode material for optoelectrochemistry and optoelectronics. Comparing with Si(111) substrate, ITO has no dangling bonds on the surface, so the fullerene/substrate interactions for ITO should be much lower than that for silicon substrate. With the PVD of C_{60} molecules being performed on this substrate, the surface mobility of C_{60} would increase and the interaction between C_{60} molecules dominates the fullerene film formation, leading to larger C_{60} polycrystalline grains. As shown in Fig. 3(a), SEM study revealed that the typical fullerene grain size is ca. $1\text{ }\mu\text{m}$.

XRD spectrum of this sample is shown in Fig. 3(b). It was observed that in this case the relative intensity of low index facet (111) to high facets (220) and (311) increases largely comparing with that on silicon surface. Moreover, it was observed that the peak line widths of C_{60} XRD spectrum in Fig. 3(b) are narrower than that in Fig. 2(d). According to the Scherrer equation:

$$t(\text{size}) = \lambda / (B \cdot \cos \theta)$$

where B is the line width of the relevant XRD peaks, which is in reverse ratio to the polycrystalline size t . Therefore, the

Fig. 3 SEM and XRD spectrometry study of the C₆₀ deposition on ITO surfaces. (a). SEM images of C₆₀ film. (b). XRD pattern correspond to C₆₀ film on ITO surface.

Fig. 4 SEM and XRD spectrometry study of the C₆₀ deposition on Cu surfaces. (a). SEM images of the sample with C₆₀ deposition on Cu surfaces. (b). XRD pattern correspond to C₆₀ film on Cu surface, no C₆₀ crystalline structure is observed.

C₆₀ grain size on ITO substrate is larger than that formed on Si(111) substrate.

Above results clearly show that smaller fullerene-substrate interaction would lead to larger polycrystalline grains of C₆₀. Next, we would like to see what's happen in the case of very strong substrate/fullerene interactions. As studied before,²¹⁾ the interaction between C₆₀ and Cu substrate is so strong that would induce essential charge transfers from the Cu substrate to C₆₀, i.e., ca. 1.6 electrons/C₆₀ molecule charge transfer was observed while C₆₀ adsorbing on the terrace of Cu substrate. So a Cu plate was selected as the third substrate.

The SEM and XRD studies of C₆₀ film depositing on Cu are shown in Fig. 4. Fascinatingly, no regular C₆₀ morphology and polycrystalline structure were observed on the Cu substrate after the PVD process, even though the experimental conditions on Cu substrate are identical to that on ITO and silicon substrates. XRD spectrometry was performed and revealed that the lack of any C₆₀ crystalline peaks too, so the C₆₀ molecules were suggested to polymerize on the copper surface. To confirm the irreversible chemical reaction of C₆₀ molecules on Cu substrate, the fullerene film was further treated up in toluene with sonication, and it is indeed that no any soluble C₆₀ was found and the film remained on Cu plate, while the C₆₀ films on ITO and Si

substrates in parallel experiments were completely re-dissolvable in toluene. Moreover, laser desorption mass spectrometry study for the C₆₀ films on Cu plate showed weak C₆₀ peak, indicating that the basic structure of C₆₀ is maintained. Therefore, C₆₀ must be polymerized on the Cu substrate under current experimental conditions.

Note that in our experiment the measured substrates' temperature is only 350–370°C, so it reminds us that copper must be an excellent catalyst for the C₆₀ polymerizing reaction. We suggest that the charge transfers between C₆₀ and substrate play a main role in the C₆₀ polymerizing reactions. Further experiments are on progress to explore the catalyzing function of Cu in fullerene polymerizations.

4. Conclusions

C₆₀ deposition on Si(111), ITO, and Cu substrates were studied by the physical vapor deposition technique. For C₆₀ deposition on Si and ITO substrates, van der Waals interactions dominate the fullerene/substrate interactions and C₆₀ molecules form polycrystalline structures, with the typical polycrystalline grain size being 0.5 and 1 μm on Si and ITO substrates, respectively. For C₆₀ molecules deposition on copper substrate, irreversible C₆₀ polymerization was

occurred under very low temperature (350–370°C), suggesting that copper is excellent catalyst for C₆₀ polymerizing reaction.

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