Journal of Crystal Growth 429 (2015) 35–42

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Temperature-dependent orientation study of the initial growth of pentacene on amorphous SiO_2 by molecular dynamics simulations

Yuanqi Zeng, Bo Tao*, Jiankui Chen*, Zhouping Yin

State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R. China

ARTICLE INFO

Article history:
Received 27 January 2015
Received in revised form
23 July 2015
Accepted 30 July 2015
Communicated by: M. Uwaha
Available online 7 August 2015

Keywords:
A1. Computer simulation
A3. Physical vapor deposition processes
B1. Organic compounds (pentacene)
B3. Field effect transistors
(Substrate temperature)

ABSTRACT

Temperature-dependent molecular orientations in the initial growth processes of pentacene on amorphous SiO_2 surface with different substrate temperatures have been investigated using molecular dynamics simulations. As the substrate temperature ranges from 270 K to 600 K, there exists a transition behavior for pentacene cluster from the normal-oriented, ordered configuration to the lateral-oriented, disordered one as measured by the decreased average orientation angle and order parameter, showing the significant effect of the substrate temperature on the molecular orientation. The transition behavior is related to the strength relationship between molecule–molecule interactions and molecule–substrate interactions. During the optimal temperature range between 300 K and 350 K, the pentacene molecules tend to form the normal-oriented, well-ordered cluster driven by the dominant molecule–molecule interactions, which is affected by the substrate temperature in a greater degree than the molecule–substrate interactions. When the temperature is lower than 300 K, the ordering of pentacene cluster becomes a little worse. A higher substrate temperature results in the lateral orientation with the weakening of the molecule–molecule interactions. Then the further intensification of molecular thermal motion gradually makes the molecules separate from the cluster or the substrate surface, resulting in the appearance of the undesirable separated configuration.

1. Introduction

Recently, organic thin film transistors (OTFTs) have been actively investigated for the microelectronic devices due to their potential for low-cost, facile manufacturing [1–3]. In particular, pentacene ($C_{22}H_{14}$) is one of the most prominent conjugated organic materials used in OTFTs because of its remarkably high charge-carrier mobility, which is strongly affected by the molecular orientation of pentacene [2,4–6]. The thin film of pentacene takes a normal orientation (the molecular long axis vertical to the substrate) or a lateral orientation (the molecular long axis parallel to the substrate). The former orientation with maximum π–π overlap is desired for pentacene OTFTs to facilitate an isotropic electric transport from source to drain parallel to the gate electrode, as depicted in Fig. 1 [7–8]. In particular, several factors can influence the molecular orientation, such as molecular number [9–11], substrate material [2], and substrate temperature [12–13]. We have theoretically investigated the molecular orientation of pentacene on amorphous SiO_2 (a-SiO_2) substrate [14]. It is found that the initially grown lateral-oriented pentacene cluster will transfer to the normal-oriented one at a critical molecular number and the existence of the sylanol groups on the a-SiO_2 surface will increase the critical molecular number. Hence, controlling and optimizing the molecular orientation is essential to achieve high device performance for OTFT devices.

The molecular orientation of pentacene thin film is known to change with the substrate temperature during the deposition process [2,15]. A considerable amount of work on the substrate temperature has been carried out recently. Dimitrakopoulos and co-workers investigated the structure order and field-effect mobility of pentacene thin film with different substrate temperatures using X-ray diffraction [16–17]. They demonstrated that a very well-ordered film is deposited when the substrate temperature is held at room temperature, higher substrate temperature induces the lower mobility resulting from the coexistence of two phases, and lower substrate temperature results in an amorphous film. Street et al. concluded that enhanced substrate temperature will lead to an increase of the crystal size of pentacene and a further increase ($>$ 363 K) leads to no growth of pentacene on the substrate [18]. Bouchoms et al. reported that the pentacene bulk phase sets in after a critical thickness of the thin film phase, which is strongly dependent on the substrate temperature, and the XRD results they obtained show that the thin film phase is a substrate induced phase and the critical film thickness will decrease with increasing substrate temperature [19]. Their experiments indicate that the order and orientation of pentacene film will change with the substrate

---

* Corresponding authors.
E-mail addresses: taobo@mail.hust.edu.cn (B. Tao), ChenJk@mail.hust.edu.cn (J. Chen).

http://dx.doi.org/10.1016/j.jcrysgro.2015.07.033
0022-0248/

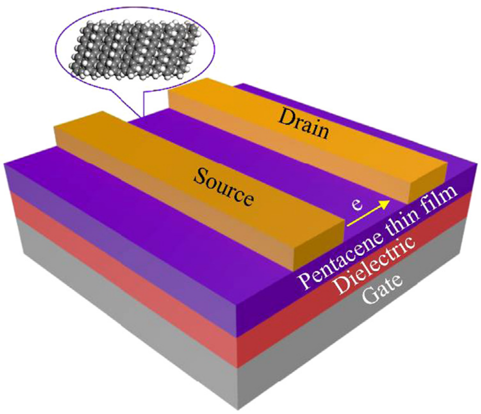

Fig. 1. In pentacene OTFT, pentacene molecules should be oriented in a normal orientation to facilitate an isotropic electric transport from source to drain parallel to the gate electrode.

temperature during the deposition process, so there should set a reasonable temperature range to help the formation of well-ordered film with desired orientation. However, this issue has not yet been fully elucidated. On the other hand, many computational calculations have demonstrated that molecular dynamics (MD) simulation is a well-known tool to investigate molecular behavior and it can provide valuable microscopic information to understand the mechanism of the growth of thin film [20]. Fichthorn and co-workers used MD simulations to study the melting of pentane, whose results of the temperature-dependent structures and the melting temperatures agree well with experiment [21]. Besides, Yoneya et al. have found that the low-temperature polymorph of pentacene thin film is unstable, and tends to transform into the high-temperature polymorph by MD simulations [22]. Mavrantzas used MD simulations to study the dependence of configurational properties of regioregular poly-3-hexylthiophene (P3HT) on temperature. They found that when the temperature was lowered below approximately 300 K, the disordered state of P3HT was found to exhibit a transition from a pure amorphous phase to a semicrystalline one [23].

These results, both experimental and computational, state briefly that the substrate temperature plays such an important role in the formation of films. Given that, the objective of this work is to study how the substrate temperature influences the molecular orientation and determine an optimal temperature range for the growth by means of MD simulations. In fact, limited by the slab size and time of the simulations, there is indeed a gap between the simulated sparse cluster and the practical condensed thin-film. Even so, as a well-known important research approach, molecular simulation can provide valuable insight into the molecular-scale mechanism with little hindrance, which experiment cannot emulate. It makes that the molecular simulation is often used to explain experimentally observed phenomena and predict the outcome unexplored by experiment. Besides, it's noticeable that the initial growth plays a decisive role in the subsequent growth, even determines the quality of the thin film. However, due to the limitations of space and time scales of experimental observation, it's difficult to explore the initial growth in directly. Here, our aim is attempt to qualitatively analysis the influence of substrate temperature on the initial growth process from the microscopic view by proposing the molecular simulations. In order to investigate it, we study the molecular orientation and order of pentacene cluster on a-SiO$_2$ substrate using MD simulations. A wide range of temperatures from 270 K to 600 K are set. Within the substrate temperature range, we find that there exists a transition for pentacene molecules from the normal-oriented, ordered phase to the lateral-oriented, disordered one during the deposition process and an optimal temperature range is obtained, which agrees well with the experimental study [24]. A comparison of the interactions between molecule–substrate and molecule–molecule is also made to elucidate the temperature-dependent orientation transition mechanism. Our results may enrich the information on the initial growth of pentacene thin film to fabricate well-ordered configuration with desired orientation.

2. Simulation methods and details

The a-SiO$_2$ substrate is prepared as an area of 64.2×64.2 Å^2 with a thickness of approximately 15.6 Å, and a vacuum of 40 Å is enlarged in the z-direction of the simulation box where the pentacene molecules can move. In practice, it is well-known that the a-SiO$_2$ substrate obtained by thermal oxidation of Si will be covered by sylanol groups (Si–O–H). To reflect the situation more realistically, all top surface Si atoms of the a-SiO$_2$ substrate are terminated with –OH groups. As we describe above, there exists a gap between the simulated sparse clusters and the practical condensed thin film. With regard to this and in order to elucidate the influence of the substrate temperature on the order of pentacene thin film more credible, two independent model systems of pentacene on a-SiO$_2$ are constructed for comparison. The first model contains 24 pentacene molecules on a-SiO$_2$ and the other one with 30 pentacene molecules, corresponding to the coverage from 0.7 to 0.9 ML (monolayer, is given in units of completed monolayer of lying pentacene, 1 ML corresponds to 34 molecules). We expect that it can prove that the influence of the substrate temperature is no coincidence through comparatively analyzing the influence of the substrate temperature on these two independent systems. The pentacene molecules depositing on sylanol-saturated a-SiO$_2$ substrate prefer to form normal orientation when the cluster size is larger than 22 [14], so the initial pentacene configurations of the two systems are constructed in the normal orientation, as shown in Fig. 2. The time of each simulation is 5 ns to ensure that the pentacene molecules have sufficient time to achieve the equilibrium shape and the data production time is 200 ps. All of the MD simulations were performed using the DISCOVER code [25], and both compounds are described using the COMPASS force field [26]. Details in calculations method were described in our previous work [14].

3. Results

To gain insight into the influence mechanism, we calculated two different quantities to characterize the orientation and order of pentacene molecules: the average orientation angle (θ) and the order parameter (OP_φ). Besides, given that the interplay between molecule–substrate interaction (E_{m-s}) and molecule–molecule interaction (E_{m-m}) is the key parameter in the self-assembly process of the nucleation and thin film growth [3], these interaction energies are used to describe the simulation results as well, which are defined as:

$$OP_\varphi = \frac{1}{2}\langle 3\cos^2\varphi - 1\rangle \tag{1}$$

$$E_{m-s}(T_{sub}) = \frac{1}{N}(E_{total} - E_{sub} - E_{pen}) \tag{2}$$

$$E_{m-m}(T_{sub}) = \frac{1}{N}(E_{pen} - \sum_{1}^{N} E_m) \tag{3}$$

here θ is the angle between the long axis of individual molecule and the substrate surface, φ is the angle between the long axes of every two molecules, and the brackets operator denote an ensemble average over the data production time. The average orientation angle characters the orientation of the pentacene cluster and the order parameter quantifies the tendency of the pentacene molecules axes to be aligned in one direction to evaluate the orderliness of the pentacene cluster. For the normal orientation, the average orientation angle θ is