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Anomalous Growth Temperature Dependence of the Surface Roughness of Pentacene Thin Films

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1. Introduction

One of the main issues involved in improving the characteristics of pentacene thin-film transistors is to increase the grain size to keep the effect of grain boundary as small as possible. To solve this problem, clarifying the growth mechanism of pentacene thin film should be crucial. Although it has been reported recently that pentacene growth on Si and SiO_2 closely mimics epitaxial growth of inorganic materials[1], a quantitative study has not been reported so far and none of the activation energies involved in growth is known yet (Fig.1). Moreover controlling the surface roughness in addition to the grain size should be crucial when it is necessary to fabricate an ultrathin film to make a transistor smaller.

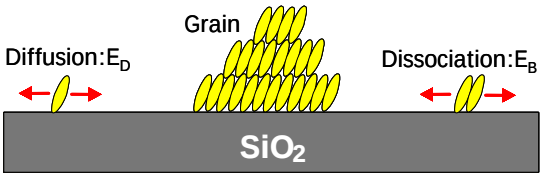

Fig.1 Schematic of the pentacene grain and elementary processes involved in the initial stage of thin-film growth. Each ellipse shows a single pentacene molecule. A surface diffusion of a molecule and dissociation of a dimer is shown together with their activation energies E_D and E_B.

In this study, we investigated the growth mechanism of pentacene thin films on SiO_2 for a wide substrate temperature range (198K to 343K) (1) to obtain activation energies involved in growth quantitatively and (2) to obtain clues to suppress surface roughness. The activation energies for surface diffusion and dissociation are obtained successfully for the first time and an anomalous growth temperature dependence of the surface roughness is observed. The importance of controlling the binding energy of molecular dimers on a substrate to suppress surface roughness is proposed. This is in contrast to the existing studies where only the importance of increasing surface diffusivity by surface treatments is stressed to increase grain size[1].

2.Experiment

Pentacene thin films with a thickness of 50nm are fabricated on thermally oxidized Si-wafers (SiO_2 thickness about 12nm) by thermal evaporation with a background pressure of 10^{-10} Torr. The deposition rate is 0.3Å/s. The substrate temperature is between 198K and 343K. The surface morphology of pentacene thin film at different temperatures are studied with atomic force microscopy (AFM) and x-ray diffraction (XRD).

3.Results and Discussion

From the XRD experiment, the diffraction of the (001) plane of the thin film phase with a spacing of 15.5 Å already appeared at 198K and the (001) diffraction of the bulk phase with a spacing of 14.5Å appeared at 332K.

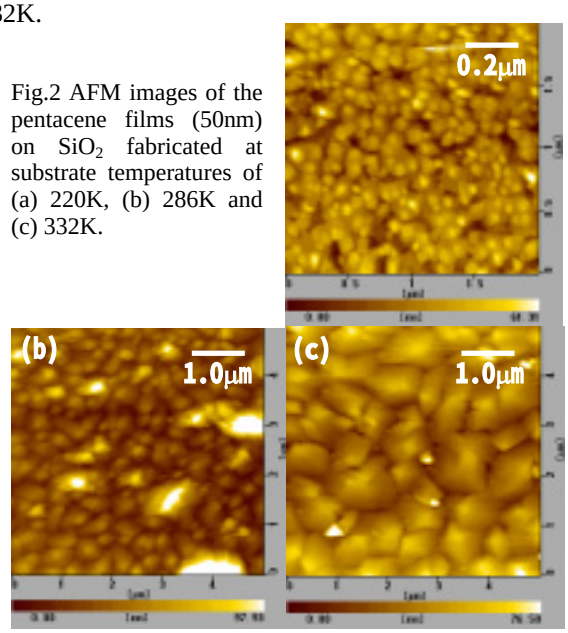

Fig.2 AFM images of the pentacene films (50nm) on SiO_2 fabricated at substrate temperatures of (a) 220K, (b) 286K and (c) 332K.

The AFM images of pentacene films prepared at different substrate temperatures are shown in Fig.2. It is seen that the grain size increases monotonically as a function of temperature, which exceeds 1 μm at 332K. The substrate temperature dependence of the grain density is summarized in Fig.3. The grain density has been evaluated by counting the number of protrusions in the image. This is supported by the fact that pentacene shows a nucleation type 3-dimensional growth[1] as is seen in inorganic epitaxial growth, which should give rise to a pyramidal shaped grain as is schematically shown in Fig.1. Therefore in the following analysis, we assume that the measured grain density can be taken as a saturation density of nucleus formed at the initial stage of growth. In fact, this is supported by the fact that the grain density of a 12.5nm thick film grown at 230K is found to be the same within an error as that of a 50nm thick film.

It is clearly observed in Fig.3 that the behavior of the grain density changes abruptly at a temperature around 250K. In terms of the well known behavior of the

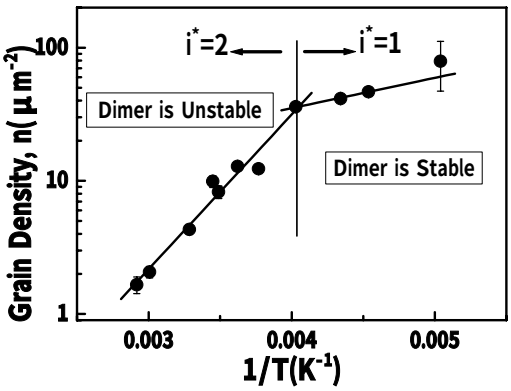

Fig.3 The grain density as a function of substrate temperature(T). i^* (critical nucleus size) changes from a single molecule to a dimer at a clear transition around 250K. Fittings in the two temperature ranges give values of 0.13eV and 0.79eV for E_D and E_B, respectively.

nucleation in inorganic epitaxial growth[2], the transition in Fig.3 can be understood as a change in critical nucleus size (i*), which is the largest unstable cluster at a given temperature, from 1 molecule below 250K to 2 molecules (dimer) above 250K. A dimer becomes unstable above this temperature, which suppresses nucleation and causes a rapid decrease in grain density. Therefore the behavior of the grain density (*n*) in the two temperature region can be fitted with the following relations.

$$n \propto \exp(-\frac{E_D}{3kT}) \qquad , i^*=1$$

$$n \propto \exp(-\frac{E_B + E_D}{4kT}) \qquad , i^*=2$$

where E_D and E_B are activation energy for surface diffusion of pentacene molecules and activation energy for dissociation of pentacene dimers, respectively. We obtain 0.13eV for E_D and 0.79eV for E_B.

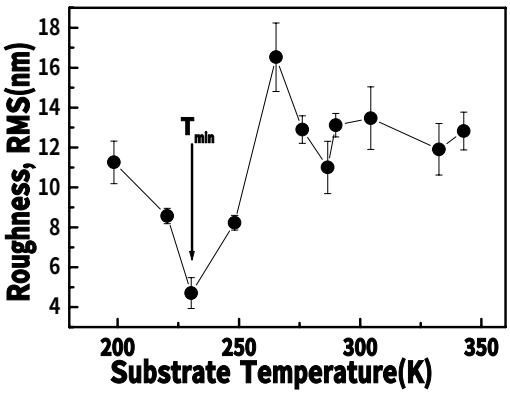

Fig.4 The surface roughness as a function of substrate temperature. Anomalous increase is observed above 230K (Tmin) giving rise to a minimum in roughness. This temperature is close to the onset of dimer dissociation indicated in Fig.3

Fig.4 shows the surface roughness of the films obtained from AFM images as a function of substrate temperature. Although the roughness is expected to decrease monotonically as the substrate temperature increases, because of the relaxation due to enhanced migration of molecules on the surface, in fact it increases from 230K to 250K, giving a minimum surface roughness around 230K(Tmin). This behavior can be attributed to the onset of pentacene dimer dissociation where the grain density starts to decrease rapidly. As shown schematically in Fig.5, the rapid decrease in grain density above Tmin leads to a rapid increase in grain size. A larger grain size causes an increase in molecular concentration on top of the grain and therefore an enhanced nucleation on the top terrace of the grain, giving rise to a rougher surface.

Therefore in order to keep the surface roughness small above room temperature, where the grain size is large, it is crucial to find a substrate or a buffer layer which increases the binding energy of pentacene dimers on a surface to shift Tmin to a higher temperature.

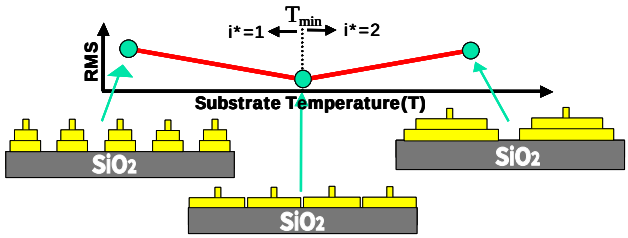

Fig.5 Schematic showing the temperature dependence of surface roughness. The figures below show the first few monolayers of pentacene for each temperature. Below Tmin, the roughness decreases as a function of temperature because of enhaced surface migration. The rapid increase in grain size above Tmin enhances nucleation on top of the grain, giving rise to a rougher surface.

4.Conclusion

The activation energies for surface diffusion and dissociation of molecular clusters are obtained successfully for the first time and an anomalous growth temperature dependence of the surface roughness is observed. From the analysis of the grain density, it is concluded that the critical cluster size changes from a single molecule to a dimer at a growth temperature around 250K. This results in a rapid decrease of the grain density above this temperature and leads to an anomalous increase of the surface roughness giving rise to a minimum in roughness. It is proposed that in order to keep the surface roughness small while maintaining a large grain size, just finding a buffer layer which increases the surface diffusivity of the molecule, as is usually done, is not enough and it is crucial to control the binding energy of pentacene molecular clusters.

References

[1] F-J. Meyer zu Heringdorf et al. , Nature **412** (2001) 517
[2] H.Brune, Surf. Sci. Rep. **31** (1998) 125