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Protrusive Morphology of Bis(triisopropylsilylethynyl)Pentacene Nanofilms Deposited on SiO_2 Surfaces via the Vacuum Thermal Evaporation Method

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Highly pure 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-PEN) nanofilms were deposited on oxidized silicon wafer substrate surfaces at two different substrate temperatures (25°C and 70°C) via the vacuum thermal evaporation (VTE) method. Atomic force and scanning electron microscope analyses showed that the TIPS-PEN films (~55 nm) prepared at two different substrate temperatures commonly have a number of protrusions widespread over the films. The protrusions, which are highly likely to be crystallites, tend to be smoother and grow higher at the elevated substrate temperature (70°C), suggesting an improved crystallinity of the film. However, this study suggests that an optimum substrate temperature higher than 70°C must be found to remove or at least minimize the protrusive morphology of TIPS-PEN semiconducting films as well as to form a perfectly polycrystalline film for an organic thin film transistor device since the morphology of a semiconductor film deeply affects the performance of a transistor.

Keywords: Triisopropylsilylethynyl-pentacene, functionalized pentacene, organic semiconductor, organic thin film transistor

1. INTRODUCTION

6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-PEN) has been of great concern as a semiconductor layer of organic thin film transistor (OTFT) devices because of its excellent electrical characteristics, mostly due to its greatly improved π-π stacking ability of TIPS-PEN molecules compared to that of un-functionalized pentacene.[1-2] Another important feature of TIPS-PEN molecules is the high solubility of them into various organic solvents, which makes possible a low cost solution process for fabricating semiconductor layers into electronic devices.[3-8] As a result, many research groups and companies are eagerly attempting to develop a solution process for depositing highly crystalline TIPS-PEN films on various substrate surfaces.[3-8] However, this simple and economic solution process suffers from considerably low reproducibility of transistor characteristics mostly due to numerous difficult quality control issues, e.g., gas-inclusion into films, solvent purity, and film thickness control. On the other hand, vacuum thermal evaporation (VTE) for depositing organic semiconductors is a highly reproducible and most reliable method already verified in electronic industries, even if this method is not so cost-effective.[9-10] In fact, in many cases, organic semiconductor layers of OTFT devices deposited by the VTE method generally show better charge carrier mobility as well as reproducibility than those prepared by solution processes do.[9-10] In addition, another considerable advantage is that the VTE method can promptly and properly reuse a great deal of evaporation equipment that has operated in modern fabrication facilities.

To date, many studies have focused on the morphology and growth of TIPS-PEN films deposited on silicon oxide surfaces by various solution processes, including spin and drop casting methods.[5,11,12] On the other hand, almost no one study has reported the morphology and growth of TIPS-PEN films deposited on silicon oxide surfaces by the VTE method[13,14] even if this information is imperative for the optimizing deposition condition of a high quality TIPS-PEN film. Therefore, in this study, we investigated the morphology and crystallinity of TIPS-PEN nanofilms deposited on silicon oxide surface by the VTE method, particularly at two different substrate temperatures (25°C and 70°C). This investigation was intended to explore how the substrate temperature affects the morphology and crystallinity of TIPS-PEN films on silicon oxide surfaces. It revealed that TIPS-PEN nanofilms have a number of unusual protrusions widespread over the silicon oxide surface at up to 70°C of the

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substrate temperature.

2. EXPERIMENTAL

All reagents were purchased from the Aldrich Chemical Co. (Milwaukee, WI) except 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-PEN). TIPS-PEN was synthesized as described in a previous publication.[1] A nuclear magnetic resonance (NMR) measurement and gas chromatography (GC) analysis were carried out to check the purity of TIPS-PEN. These analyses revealed that the purity is at least above 99%. Figure 1 shows a NMR spectrum for TIPS-PEN molecules, and its peak positions exactly match with previously reported data.[1]

The oxidized (100) Si wafer (1.5 cm×1.5 cm) was soaked in a piranha solution for ten minutes and was then sonicated in ultra-pure water for five minutes to remove any organic contaminants that may have been on the surface. The cleaned Si wafer substrate and TIPS-PEN source were placed in a chamber together at 7×10^{-6} torr of vacuum pressure. After that, TIPS-PEN was directly evaporated onto the oxidized Si wafer surface at a source temperature of 80°C. Upon evaporation, the substrate temperature was maintained either at 25°C or at 70°C. The evaporation rate was at least faster than 1.0 Å/sec. Atomic force microscopic images were probed with an SPA 400 (Seiko, Japan; tapping mode, scan speed: 0.5-0.6 Hz, scan size: 10×10 μm). Field emission-scanning electron microscopic images were taken with a JSM-7401F (JEOL Corp., Japan; cold tip field emission) at room temperature with a magnification of 20,000 times. No conductive Pt coating was applied to the sample surface. The electron beam was at normal incidence to the sample, and the accelerating voltage was 1.0 kV.

3. RESULTS AND DISCUSSION

Two different TIPS-PEN nanofilms (~55 nm) were deposited on oxidized silicon wafer surfaces at the substrate temperatures T_s = 25°C and 70°C, respectively. Then, the film surfaces were imaged with an AFM (SPA 400, Seiko, Japan), and these images are shown in Fig. 2. Interestingly, these images commonly show a number of protrusions grown on silicon oxide surface. In particular, the image in Fig. 2(a), which is a TIPS-PEN nanofilm prepared at T_s = 25 °C, shows so many TIPS-PEN protrusions nearly entirely covering the substrate surface (RMS = 8.68 nm). These pro-

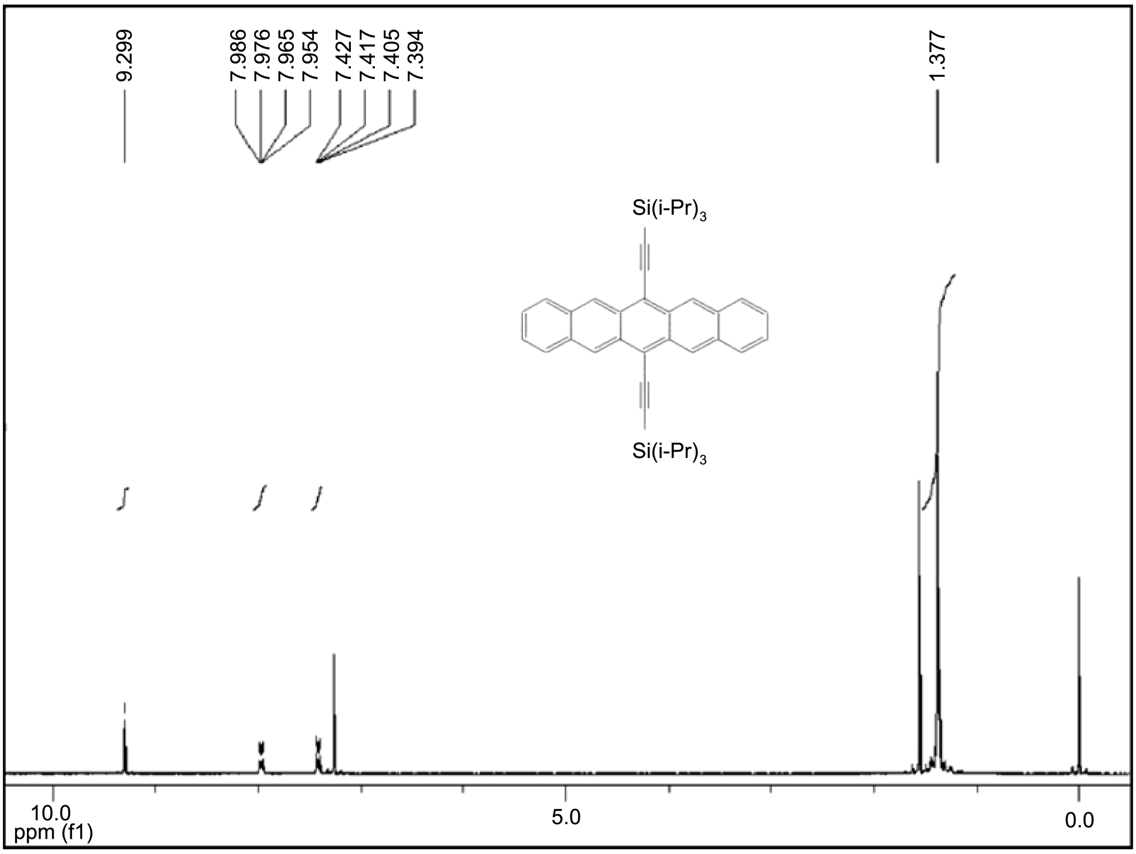


Fig. 1. A ^{1}H nuclear magnetic resonance (NMR) spectrum of 6,13-bis(triisopropylsilylethynyl)pentacene (300 MHz, $CDCl_3$): 1.38 (s, 42H), 7.41 (dd, J = 6.6, 3.0 Hz, 4H), 7.97 (dd, J = 6.6, 3.0 Hz, 4H), 9.3 (s, 4H). The product was synthesized from 6, 13-pentacenequinone to give a 50% yield of dark blue fin-shaped plates.

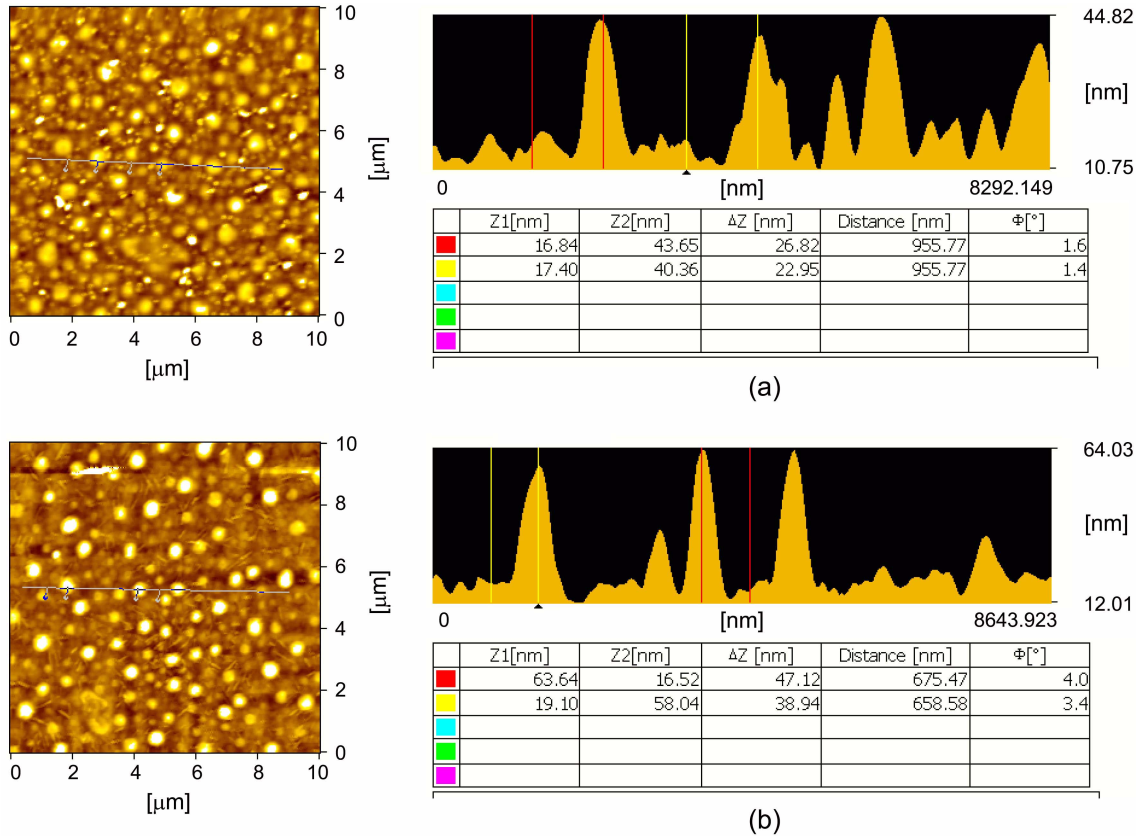
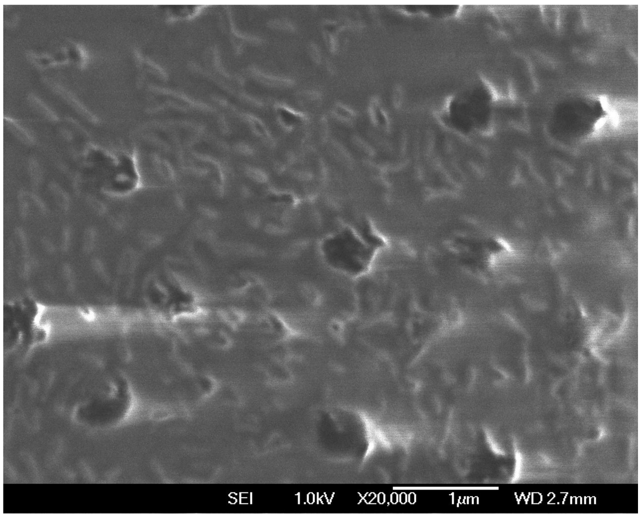


Fig. 2. Atomic force microscopic images of TIPS-PEN nanofilms deposited on oxidized silicon wafer substrate surface via the VTE method. (a) A TIPS-PEN nanofilm prepared at T_s = 25°C; P_{vap} = 7 × 10^{-6} torr; T_{source} = 80°C; R_{evap} ≥ 1.0 Å/sec (RMS = 8.68 nm). (b) A TIPS-PEN nanofilm prepared at T_s = 70 °C; P_{vap} = 7 × 10^{-6} torr; T_{source} = 80°C; R_{evap} ≥ 1.0 Å/sec (RMS = 10.43 nm). The lines drawn on the images represent z-axis profiles of the films, and the profiles and tables (scale information) are shown on the right side of the images. It is important to note that the protrusions are generally higher (Δ ~ 20 nm), but the rest of the film surface is smoother in the case of a heated substrate sample (b) than in the unheated case (a).

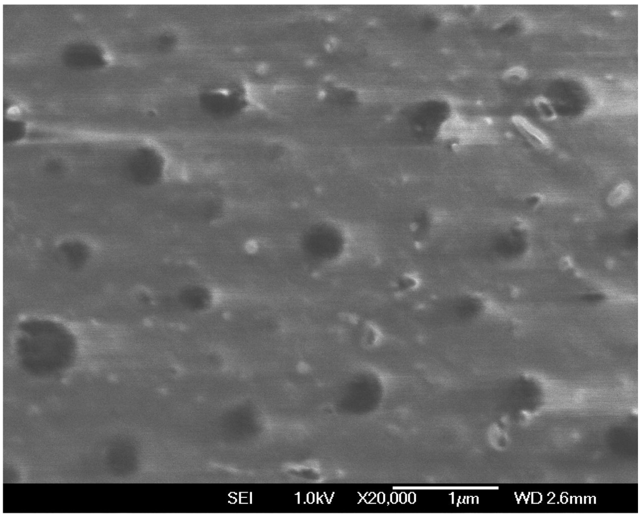
trusions typically have approximate heights of 40 nm and widths of 600 to 900 nm. In contrast, a TIPS-PEN nanofilm prepared at T_s = 70°C (Fig. 2(b)) has relatively less dense but higher (~60 nm heights) and narrower (500 ~ 600 nm widths) protrusions, which gives rise to a higher RMS roughness (10.43 nm). As the line profiles in Fig. 2 indicate, the TIPS-PEN protrusions in the heated substrate case (Fig. 2(b)) are generally 20 nm higher than those in the unheated case (Fig. 2(b)). In addition, the line profiles in Fig. 2 clearly show that the rest of the surface domains except the protrusions are smoother in the heated substrate case (2(a)) than in the unheated case (2(a)) even if the heated case has a larger RMS roughness value (10.43 nm) than the unheated case does (8.68 nm).

In order to visually observe the protrusions, photographs of the TIPS-PEN nanofilms were taken with an FE-SEM (JSM-7401F, Jeol, Japan), and the images are shown in Fig. 3. As shown in Fig. 3(a), irregular dark regions represent the TIPS-PEN protrusions. The remaining area except the protrusions in Fig. 3(a) also has so many tiny protrusions, indicating that the surface is considerably rough. On the contrary, the protrusions on the unheated substrate surface have nearly circular shapes, as shown in Fig. 3(b). The image 3(b) further shows that the remaining surface except the protrusions is considerably smoother than the similar area in the unheated case. These results strongly suggest that TIPS-PEN film tend to grow on the heated substrate surface at least partially in an ordered manner when the protrusions develop. The rougher and more irregular morphology of a TIPS-PEN nanofilm deposited on an unheated silicon oxide substrate surface suggests the completely amorphous growth of the film, whereas relatively the smoother morphology and circular-shaped protrusions in the heated substrate case clearly support at least the partial crystalline growth of the film. This hypothesis is also firmly supported by the fact that the elevated substrate temperature improves the crystallinity of the film prepared by the VTE method.[9-10]

Another noteworthy point in this study is the existence of protrusions formed on the silicon oxide surface at a substrate temperature of up to 70°C. In fact, Ostroverkhova *et al.*[13]



(a)



(b)

Fig. 3. Field Emission-Scanning Electron Microscopic (FE-SEM) images of TIPS-PEN nanofilms deposited on oxidized Si wafer surfaces at T_s = 25°C (a) and 70°C (b). The protrusions in the heated case (b) have much more regular or circular shapes than in the unheated case, and the rest of the film domains have a smoother morphology in the heated case (b) than in the unheated case.

recently reported the existence of the protrusions of a TIPS-PEN film evaporated on a glass substrate at T_s = 25°C. The aforementioned authors claim that the protrusions are crystallites, but the rest of the film is predominantly amorphous. Indeed, this claim matches well with our results. However, it is also interesting to note that the protrusive morphology was gone from a TIPS-PEN film evaporated on a glass substrate at T_s = 85°C. Instead, Ostroverkhova *et al.*[13] showed that the film is predominantly polycrystalline via the x-ray diffraction analysis, mainly due to the elevated substrate temperature. This may suggest that the substrate temperature used in this study (T_s = 70°C) is not high enough to suppress the formation of the discrete crystallites or protrusions as well as to promote the formation of a complete polycrystalline film. Therefore, it is imperative to know what substrate temperature higher than 70°C is optimum for the formation of a perfectly polycrystalline TIPS-PEN film, and the investigation is currently underway.

4. CONCLUSIONS

In this study, considerably protrusive morphologies of highly pure TIPS-PEN nanofilms evaporated on oxidized silicon wafer substrates via the VTE method were identified at various substrate temperatures of up to 70°C. AFM and FE-SEM analyses reasonably support that the protrusions are discrete crystallites, which means that the rest of the film is highly likely to be amorphous. However, the smoother morphology and circular shapes of the protrusions in the heated substrate case strongly indicate that the elevated temperature tends to promote a crystalline ordering of TIPS-PEN molecules on silicon oxide surface. Nevertheless, it is essential to find an optimum substrate temperature which can completely remove or noticeably diminish the protrusive morphology of TIPS-PEN semiconducting films, as well as which can promote the formation of a perfectly polycrystalline film for OTFT devices since the morphology of an organic semiconductor film deeply affects the performance of a transistor.

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REFERENCES

1. J. E. Anthony, J. S. Brooks, D. L. Eaton, and S. R. Parkin, *J. Am. Chem. Soc.* **123**, 9482 (2001).
2. J. E. Anthony, D. L. Eaton, and S. R. Parkin, *Org. Lett.* **4**, 15 (2002).
3. S. K. Park, T. N. Jackson, J. E. Anthony, and D. A. Mourey, *Appl. Phys. Lett.* **91**, 063514 (2007).
4. J. G. Park, R. Vasic, J. S. Brooks, and J. E. Anthony, *J. Appl. Phys.* **100**, 044511 (2006).
5. Y. H. Kim, Y. U. Lee, J. I. Han, S. M. Han, and M. K. Han, *J. Electrochem. Soc.* **154**, H995 (2007).
6. J. H. Kwon, J. H. Seo, S. I. Shin, K. H. Kim, D. H. Choi, I. B. Kang, H. Kang, and B. K. Ju, *IEEE Trans. Electron Devices* **55**, 500 (2008).
7. S. K. Park, J. E. Anthony, and T. N. Jackson, *IEEE Electron Device Lett.* **28**, 877 (2007).
8. W. H. Lee, D. H. Kim, Y. Jang, J. H. Cho, M. Hwang, Y. D.

Park, Y. H. Kim, J. I. Han, and K. Cho, *Appl. Phys. Lett.* **90**, 132106 (2007).
9. J. Locklin, M. E. Roberts, S. C. B. Mannsfeld, and Z. Bao, *J. Macromol. Sci.* **46**, 79 (2006).
10. A. C. Mayer, J. M. Blakely, and G. G. Malliaras, *Organic Field Effect Transistors* (eds., Z. Bao and J. Locklin), pp. 341-369, CRC Press, Boca Raton, FL (2007).
11. J. Chen, D. C. Martin, and J. E. Anthony, *J. Mater. Res.* **22**, 1701 (2007).
12. J. Chen, J. Anthony, and D. C. Martin, *J. Phys. Chem. B* **110**, 16397 (2006).
13. O. Ostroverkhova, S. Shcherbyna, D. G. Cooke, R. F. Egerton, F. A. Hegmann, R. R. Tykwinski, S. R. Parkin, and J. E. Anthony, *J. Appl. Phys.* **98**, 033701 (2005).
14. C. D. Sheraw, T. N. Jackson, D. L. Eaton, and J. E. Anthony, *Adv. Mater.* **15**, 2009 (2003).