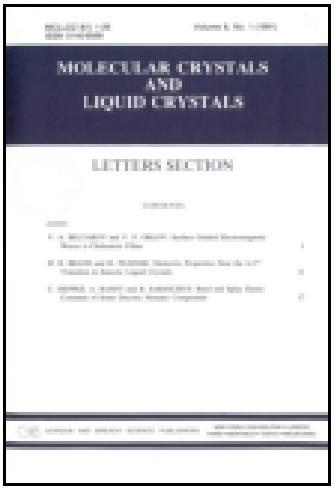

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Effects of Annealing on the Mechanical Properties of Pentacene and Tris(8-hydroxyquinoline) Aluminum Films

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Annealing is reported as an effective process to improve electrical properties of organic semiconducting films. The mechanical properties of pentacene and tris(8-hydroxyquinoline) aluminum (Alq_3) films annealed at 140°C were investigated in this study by nanoindentation testing. AFM observations of as-coated and annealed pentacene films indicate grain growth from 160 to 258 nm. The annealing process decreases pentacene and Alq_3 film hardness by 23 and 36% from those of the as-coated films, 0.643 and 0.523 GPa. Grain growth and decreasing hardness are attributed to thermal diffusion and recrystallization of molecules.

Keywords organic semiconducting film; annealing; nanoindentation; mechanical property; morphology; grain growth

1. Introduction

Organic semiconducting films (OSFs) are attractive prospective materials for electroluminescence (EL) devices, transistors, and solar cells because of their electrical features. Additionally, OSFs contain superior mechanical flexibility and have low manufacturing costs compared to current inorganic silicon semiconductors. However, the electrical properties of OSFs are still apparently lower than those of silicon. As a result, attempts have been carried out to improve these electrical properties via annealing [1, 2]. Pentacene is the most promising candidate for organic transistors, due to its high carrier mobility. Kang *et al.* [3] examined the *in situ* postannealing effects on polycrystalline pentacene transistor films grown in an ultrahigh vacuum atmosphere. Their studies showed improved field effect mobility of the films from 0.19 to 0.49 cm^2/Vs. In addition to Kang's work, further studies [4–8] have confirmed the improved mobility of annealed pentacene transistors under suitable annealing conditions including temperature, substrate, and atmosphere.

In contrast to electrical properties, the annealing effects on the mechanical properties of OSFs have not been elucidated, even though the mechanical properties of flexible OSFs

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are very important in designing semiconducting devices. The authors [9–11] have examined the mechanical properties of some OSFs, including pentacene film, using nanoindentation (NI) testing and suggested a prediction equation of a critical bending radius at which OSF is plastically broken under a bending stress. In the present study, nanoindentation (NI) tests and atomic force microscope (AFM) measurements were conducted to investigate the mechanical and topographic properties of annealed pentacene films. In addition, the mechanical properties of annealed tris(8-hydroxyquinoline) aluminum (Alq_3) film was also measured to reconfirm ubiquitous results obtained with the pentacene films.

2. Experiment

Pentacene and Alq_3 films were coated on BK-7 glass substrates (indentation hardness of 6.0 GPa) by vacuum evaporation. Conditions ideal for the substrate were employed at room temperature, with an evaporation rate of 0.15–0.3 nm/s, and a vessel pressure of 10^{-4} Pa. The films were annealed at 140°C for 12 h at an inert nitrogen gas flow of 1.5*l*/min in a vessel volume 2.4*l*. The annealing conditions employed in this study (high temperature and prolonged experimental time) are consistent with previous studies [3–8]. These conditions were selected intentionally due to the measured annealing effects on the mechanical properties of OSFs. Specifically, the annealing temperature attains a rate of 0.72 to the melting point of pentacene T_M and is beyond the phase transition temperature of the pentacene material 124°C [12]. In preliminary experiments, a pentacene film was additionally annealed at 140°C for 8 h. These conditions confirmed no annealing effects on indentation hardness due to the thermal stability of the film.

Film thickness was measured by employing the indentation method. The surface topography of pentacene films was examined via AFM (Digital Instruments Nanoscope E) in contact mode. The NI tests were conducted using a load range of 0.04–1 mN, with a penetration rate of 0.5–2 nm/s. Tests were conducted with an in-house-developed tester, controlled by an indentation process of stepwise displacement. For each load, the NI tests were repeated twice at five different points on the film surface, to confirm there was no thermal drift of the testing system. Detailed procedures regarding coating, thickness measurements, and calculating mechanical properties have been described in our previous papers [9, 11].

3. Results and Discussion

Prior to AFM measurements, the as-coated and annealed pentacene films were observed with an optical microscope. Optical microscopy revealed the formation of large-scale ridge structures; typical of substances dewetted from the substrate [7]. Figure 1 shows

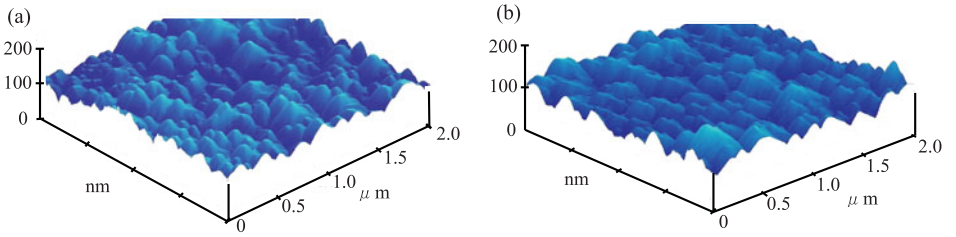

Figure 1. AFM images of (a) as-coated and (b) annealedpentacene films. Average grain sizes are calculated as 160 nm for the as-coated film and 258 nm for the annealed film.

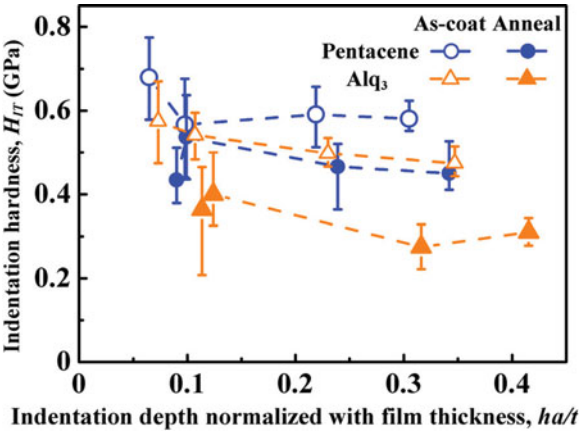

Figure 2. Indentation hardness, H_{IT} of pentacene and Alq_3 films measured prior to and after annealing. Values are plotted against indentation depth normalized by film thickness h_a/t.

AFM topographic images of (a) as-coated and (b) annealed pentacene films; composed of polycrystalline grains. Comparing the images, it is evident that the grains on the annealed film are larger than those on the as-coated film. The average grain sizes were calculated as 160 nm for the as-coated film and 258 nm for the annealed film from the cross-sectional profiles. Arithmetic mean surface roughness of the annealed film is inversely reduced from 3.36 nm to 2.21 nm relative to the grain size. The grain growth of pentacene crystals arises from molecular thermal diffusion followed by recrystallization. Diffusion velocity exponentially accelerated with increasing temperature. Therefore, it may be stipulated that the current annealing temperature of $0.72T_M$ is enough for the pentacene films to recrystallize. Kang *et al.* [3] found gradual grain growth with the elimination of defects and misoriented crystallites as the annealing temperature was increased to 90°C. Furthermore, Fukuda *et al.* [8] annealed a pentacene film coated on a silicone oxide substrate at 140°C for 1 h and found the structure of the film changed from thin-film phase to bulk phase during the annealing process.

The thicknesses t of the pentacene films were the same prior to and after the annealing process (870 nm). Thus, no significant amount of desorption occurred during the annealing process. On the other hand, the thickness of the Alq_3 annealed film was reduced from 1150 nm to 980 nm by a factor of 15%, indicating large desorption. Figure 2 shows indentation hardness H_{IT} of pentacene and Alq_3 films measured before and after annealing. The hardness was plotted against indentation depth, normalized by film thickness h_a/t. The H_{IT} values of annealed pentacene and Alq_3 films are consistently lower than those of the as-coated films. On average, the indentation hardness is determined as 0.497 and 0.337 GPa for the annealed pentacene and Alq_3 films and as 0.643 and 0.523 GPa for the as-coated films. The decreasing hardness reflects recrystallization of the films, caused by thermal diffusion of the molecules during the annealing process. The as-coated films have an amorphous structure. They are typically intensely strained during the deposition as vaporized molecules/clusters arrive on the surface of glass substrate and are simultaneously trapped by quenching. The annealing process lowers yield strength/hardness of the films by recrystallizing the films and releasing the accumulated strain. Simultaneously measured indentation moduli of the pentacene and Alq_3 films were almost the same prior to and after the annealing process within acceptable data variation as summarized in Table 1. This

Table 1. Summaries of the AFM measurements and indentation tests

	Pentacene		Alq_3	
	As-coat	Annealed	As-coat	Annealed
Thickness (nm)	870	870	1150	980
Grain size (nm)	160	258	—	—
Roughness (nm)	3.36	2.21	—	—
Indentation modulus	15.2	17.3	6.48	7.09
Indentation hardness	0.643	0.497	0.523	0.337
Bending radius (mm)	4.42	6.51	2.32	3.93

stability of indentation moduli indicates there is no effect of desorption on the indentation tests of annealed films, including the Alq_3 films, in which a large thickness reduction was measured.

These elastic and plastic mechanical behaviors of the as-coated and annealed OSFs are explained according to our common sense concerning the mechanics of materials [13] as shown in Fig. 3. While OSF molecules (colored circle) arrayed in a crystalline structure (a) are strained due to a tensile stress σ, the molecules are elastically extended to the strained direction (b) with depending on the indentation modulus E_{IT}. And shear

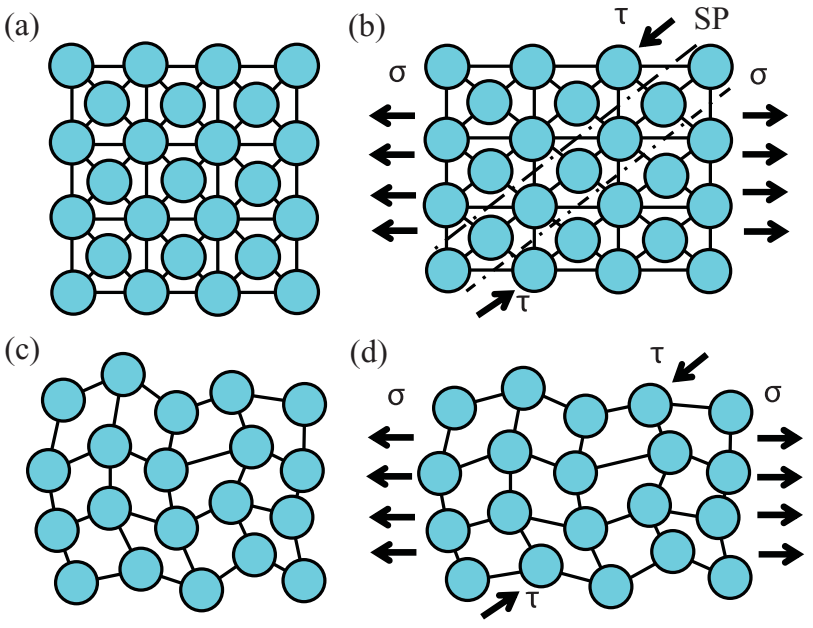

Figure 3. Schematic drawings of molecular arrays and their deformations. When molecules arrayed in a crystalline structure (a) or an amorphous structure (c) are strained with a tensile stress σ, molecules are extended with depending on the indentation modulus E_{IT} in the strained direction(b)(d). And simultaneously with the tensile stress, shear stress τ arises in all the inclined directions to tensile stress.

stress τ simultaneously arises in the inclined direction to the σ. In the case of an amorphous structure (c)(d), elastic strain of OSF occurs in the same manner as the case of the crystalline molecules. It is well understood that the indentation moduli of the as-coated films and the annealed films are not greatly different in the present study in spite of the different packing ratios (PRs). This is because bonding force between molecules which directly relates to the elastic behavior is almost independent from molecular structures, crystalline or amorphous, such as the case between austenitic steels arrayed in the face-centered-cubic structure (PR = 74%) and ferritic steels arrayed in the body-centered-cubic structure (PR = 68.0%). When once the σ is beyond a yield strength σ_y of the crystalline OSF, the molecules begin to plastically slip due to the τ along slip planes (SP) on which a group of molecules orderly forms a flat plane as shown in Fig. 3(b). Additionally an actual σ_y is considerably decreased than a theoretical σ_y by the motion of dislocations. However a resistant force of the amorphous molecules against slipping is much larger than that of the crystalline molecules because the amorphous molecules which have no flat slip plane are impossible to easily move as shown in Fig. 3(d). Therefore the σ_y of the amorphous molecules are larger than that of the crystalline molecules. Since the indentation hardness H_{IT} directly relates to the σ_y, it is well understood that the H_{IT} values of the annealed films decrease from those of the as-coated films in the present study.

Critical bending radius [10], during which plastic yielding of the OSFs occurs, was calculated using indentation hardness values and the indentation moduli on the assumption that the 90 nm thick OSF coated on the 125 μm thick flexible substrate was bent. The calculated critical bending radii, 6.51 and 3.93 mm, for annealed pentacene and Alq_3 films respectively, were larger than those of as-coated films, 4.42 and 2.32 mm. Therefore, the bending strength, defined as the reciprocal of the critical bending radius, decreased in both films during the annealing process. The results obtained from the AFM measurements and the indentation tests are summarized in Table 1.

4. Conclusions

The annealing effects on mechanical properties were investigated for pentacene and Alq_3 films coated on glass substrates using AFM measurements and nanoindentation testing. The AFM measurements for pentacene films showed the grain growth of the film annealed at $0.72T_M$ due to molecular thermal diffusion, followed by recrystallization of molecules. The indentation hardness of the annealed films decreased by 22.7% for the pentacene films and 35.6% for the Alq_3 films. The decreasing hardness is attributed to recrystallization, which changes the amorphous structure of the as-coated film to crystalline structure and also releases accumulated strain. The indentation moduli of the annealed films were the same as those of the as-coated films in both materials. The bending strength of annealed films decreased by 47% for the pentacene film and 69% for the Alq_3 film.

Acknowledgments

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References

[1] Wei, H., Li, J., Xu, Z., Cai, Y., Tang, J., & Li, Y. (2010). *Appl. Phys. Lett.*, *97*, 083302.
[2] Flugge, H., Schmidt, H., Riedl, T., Schmale, S., Rabe, T., Fahlbusch, J., Danilov, M., Spieker, H., Schobel, J., & Kowalsky, W. (2010). *Appl. Phys. Lett.*, *97*, 123306.
[3] Kang, S., Noh, M., Park, D., Kim, H., Whang, C., & Chang, C. (2004). *J. Appl. Phys.*, *95*, 2293.
[4] Tsao, H., & Lin, Y. (2012). *Appl. Phys. Lett.*, *101*, 113306.
[5] Guo, D., Ikeda, S., Sasaki, K., Miyazoe, H., & Terashima, K. (2006). *J. Appl. Phys.*, *99*, 094502.
[6] Takenobu, T., Watanabe, K., Yomogida, Y., Shimotani, H., & Iwasa, Y. (2008). *Appl. Phys. Lett.*, *93*, 073301.
[7] Goose, J., Wong, K., Clancy, P., & Thompson, O. (2008). *Appl. Phys. Lett.*, *93*, 183306.
[8] Fukuda, K., Sekitani, T., & Someya, T. (2009). *Appl. Phys. Lett.*, *95*, 023302.
[9] Kanari, M., Karino, Y., & Wakamatsu, T. (2005). *Jpn. J. Appl. Phys.*, *44*, 8249.
[10] Kanari, M., Kawamata, H., & Wakamatsu, T., (2007). *Appl. Phys. Lett.*, *90*, 061921.
[11] Kanari, M., Kunimoto, M., Wakamatsu, T., & Ihara, I. (2010). *Thin Solid Films*, *518*, 2764.
[12] Chen, J., Tee, C. K., Yang, J., Shaw, C., Shtein, M., Anthony, J., & Martin, D. C. (2006) *J. Polym. Sci., Part B: Polym. Phys.*, *44*, 3631.
[13] Ashby, M. F., & Jones, D. R. H. *Engineering Materials 1* (Butterworth-Heinmann, Oxford, 2012) 4th ed., chaps. 4–10.