Morphological, structural and electrical properties of pentacene thin films grown via thermal evaporation technique

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ABSTRACT

The physical and structural characteristics of pentacene thin films on indium tin oxide (ITO)-coated glass were studied. The pentacene films were deposited using the thermal evaporation method with deposition times of 20, 30, and 60 minutes. Field-emission scanning electron microscopy (FESEM) images revealed that film thickness increased with deposition time, with a bulk phase layer appearing at 60 minutes. The presence of the thin-film phase corresponding to 15.5 Å lattice spacing was demonstrated by X-ray diffraction (XRD) patterns in pentacene films with deposition times of 20 and 30 minutes. Meanwhile, with a deposition time of 60 minutes and a lattice spacing of 14.5 Å, the existence of the bulk phase was verified in the pentacene film. Atomic force microscopy (AFM) images of the crystallinity of the pentacene films revealed that the pentacene films deposited on ITO-coated glass exhibited the formation of similar islands with modular grains, results in a fine crystalline structure. From the current-voltage (I-V) and current density-voltage (J-V) characteristics, the pentacene films were ohmic and that current increased as the pentacene’s thickness decreased. Pentacene films deposited on an ITO-coated glass substrate showed potential in the development of broadband and narrowband optoelectronic devices on a transparent substrate.

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1. INTRODUCTION

In this new era of science and technology, organic electronics is experiencing rapid growth in the tremendously exciting area of research and development in organic electronics. Organic molecular crystals are assembled from the intermolecular interaction with weak van der Waals forces, and multiple crystalline packaging states commonly exist in the active layer of a semiconductor device. Pentacene (C₂₂H₁₄) is one of the p-type organic semiconductor materials that are widely used in the optical and electronics fields. It is a polycyclic aromatic hydrocarbon made up of five fused benzene rings with the appearance of purple or deep blue solid color in powder form. Nevertheless, when pentacene is exposed to light, air, or chemicals, it will change to green color due to degradation. Pentacene’s crystalline structure is triclinic, involving thin-film,
bulk, and single-crystal phases [1]. When ultraviolet (UV) or visible light is absorbed, the compound will be excited. When the number of acene rings increases, the bandgap of pentacene decreases and the temperature increases. Pentacene has unique properties compared with other linear acenes, such as benzene, naphthalene, anthracene, tetracene, hexacene, and heptacene. Among organic materials, pentacene thin films exhibit the highest mobility of up to 35 cm²/Vs [2]-[5] in transistors, lending to their potential application in inexpensive electronic devices due to their low cost [6], flexibility, large area, light weight, and low-temperature processing [7]-[9]. These materials are deposited on various substrates including silicon, transparent plastic, and glass. The fabrication of optoelectronic devices on transparent substrates such as, glass or indium tin oxide (ITO)-coated glass, is attracting interest for applications in photo-detection and photo-multiplications for broadband and narrowband response ability using organic-only or organic-inorganic heterojunction diode structures.

There are a number of deposition processes for growing pentacene thin films. From reported studies, pentacene thin films are mostly grown using physical deposition, such as thermal evaporation [7], [10]-[14], pulsed laser deposition (PLD) [15], [16], and organic molecular beam deposition (OMBD) [16], whereas chemical deposition, such as ink-jet printing, dip coating [17], and solution-based spin coating [18], depends on preparation conditions and the material’s nature. The physical evaporation techniques operate by changing the phase of the pentacene from a solid phase to the vapor phase and converting again to a solid phase on the substrate. Meanwhile, chemical deposition is strongly dependent on the chemistry of the solution, pH value, and viscosity. Soluble pentacenes, such as 6,13-bis(triisopropylsilyl)pentacene, also known as TIPS-pentacene, have gained consideration for the deposition of thin films from solutions. The selection of technique will affect the film’s quality and the overall appearance on the substrate [19].

This work reports the processes involved in the deposition of pentacene thin films via thermal evaporation, emphasizing on the inorganic conductive oxides with a transparent substrate. The influence of deposition time and film thickness with constant pentacene’s weight and vacuum pressure was discussed on the morphological and structural properties of pentacene films. Finally, we investigated the electrical properties of the pentacene thin films with varying deposition times using a metal-organic metal structure for the development of a heterojunction configuration of pentacene and conductive oxide for photo-diode applications.

2. RESEARCH METHOD

Figure 1 shows the flowchart of the deposition process of pentacene thin films on ITO-coated glass using the thermal evaporation technique. Pentacene powder (Sigma-Aldrich) was used without any other further purification. The substrate was an ITO-coated glass with sheet resistance of 10 Ω/sq cut into 1.5cm×2cm. The ITO-coated glass substrate was rinsed with acetone, methanol, and deionized water using ultrasonic bath for 10 minutes in 50 ml of each solution. Then, the substrates was dried slowly at room temperature using an air dust blower.

![Flowchart of pentacene thin film’s deposition process](image)

Pentacene in a solid or powder form was deposited on the ITO-coated glass using a thermal evaporator system (Ulvac Kiko: VPC-061), as shown in Figure 2(a). The distance between the pentacene
powder in a tungsten boat and the substrate holder was about 10 cm. The applied current was kept constant at 38 A for each deposition time of 20 min, 30 min, and 60 min to optimize the condition of the thin films at room temperature. The vacuum system’s pressure and the pentacene’s powder weight were 6.18×10⁻² Pa and 0.04 g, respectively. For electrical characterization, the top-contact was aluminium (Al). An Al wire was placed on the tungsten boat and deposited using thermal evaporation onto the pentacene thin film. Figure 2(b) shows the metal-organic-metal structure with pentacene thin film as an active layer.

The thickness of the pentacene thin film was measured using field-emission scanning electron microscopy (FESEM) (JEOL JSM-7600F) with a 15 kV accelerating voltage through the FESEM cross-section. X-ray diffraction (XRD) was used to measure the structure of the pentacene thin film using Cu Kα radiation (λ=0.154060 nm) and analyzed using HighScore software. The 2θ range was 5°-40° with slit=½ omega 0.5°. Atomic force microscopy (AFM) was used using a contact mode to examine the morphology of the grains of the pentacene on ITO-coated glass. The scan size was 1 µm and the scan was analyzed using Spisel32 software. Meanwhile, the current-voltage (I-V) and current density-voltage (J-V) measurement of the metal-pentacene-metal structure was carried out using Oriel Sol1A software.

Figure 2. Schematic diagrams of, (a) Pentacene deposited using thermal evaporation, (b) Metal-organic-metal structure with pentacene thin film as an active layer

3. RESULTS AND DISCUSSION

3.1. Characteristics of film thickness

Figure 3(a)-3(c) depict cross-sections of FESEM images of pentacene thin films at three deposition times. FESEM images revealed that film thickness increased with increasing deposition times from 20 min to 30 min and 60 min. The deposition time affected the thickness of the pentacene thin films. Figure 3(c) shows that another layer was detected, with a thickness of 131 nm, which was the bulk phase changing from the thin-film phase [1]. Figure 3(d) shows the relationship between deposition time and the thickness of the thin film. Thus, thickness increased gradually from 356 nm to 452 nm and 581 nm when the time for the evaporation process increased [20]. The longer deposition time revealed a thicker pentacene thin film.

3.2. Characteristics of the pentacene structure

Interestingly, Figure 4 reveals the presence of X-ray diffraction (XRD) patterns for pentacene thin films grown on ITO-coated glass with different deposition times. The films exhibited one phase with a peak of diffraction of the first order at 5.78°, corresponding to 15.5 Å of lattice spacing, which confirmed the thin-film phase. Furthermore, XRD indicated a second spacing of a second phase at a diffraction angle of 6.18°, corresponding to the lattice spacing of 14.5 Å. This pattern showed the presence of pentacene in the bulk phase. It showed five polymorphs, labeled as the triclinic crystalline phase, for the pentacene deposits on the ITO-coated glass substrate. (00k) represents the thin-film phase, while (00k′) represents the bulk phase. The pentacene thin film only possessed crystallinity on the (001) plane at deposition time of 20 min and 30 min.

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Figure 3. Cross-section of pentacene thin film at deposition time of, (a) 20 min, (b) 30 min, and (c) 60 min, and (d) Relationship between deposition time and thickness of pentacene thin film.

Figure 4. XRD patterns of pentacene thin film grown on ITO-coated glass with deposition time of 20 min (black line), 30 min (red line), and 60 min (blue line). The inset shows the AFM result.

However, deposition time of 60 min indicated a thin-film phase with crystallinity on the (001), (002), (003), (004), and (005) planes, and bulk phase on the (001'), (002'), and (003') planes. The bulk phase appeared by increasing the deposition time of the pentacene. When thickness increased, there was a transition from the thin-film phase to the bulk phase due to the pentacene grains being mixed by the process of reevaporation. The presence of the bulk phase strengthened the adhesion of the pentacene to the ITO-coated glass. This is also evident in other studies, which reported that the bulk phase assists the pentacene layer in its
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increased. From the resistivity measurement using the gradient of the I-V curve, the trend of the pentacene thin film’s resistivity showed an increase with the increase of the pentacene thin film’s thickness. The resistivity values were $1.72 \times 10^{10}$, $2.61 \times 10^{10}$, and $3.45 \times 10^{11} \, \Omega \cdot \text{cm}$ for pentacene thickness of 356, 452, and 712 nm, respectively. The relationship between current density as a function of the pentacene’s thickness is presented in Figure 6(b). Current density increased when the thickness was thinner with increasing forward-bias voltage.

![image](https://example.com/image)

Figure 6. These figures are, (a) Current-voltage characteristics, (b) Current density as a function of the thickness

Furthermore, current density can be determined from equation

$$J = \frac{I}{A}$$

(2)

where the largest current density of about $5.52 \times 10^{-5} \, \text{A/cm}^2$ was obtained for voltage bias of $+20 \, \text{V}$ with 356nm of thickness.

4. CONCLUSION

In summary, the pentacene’s morphological and structural studies were done with deposition time of 20 min, 30 min, and 60 min using thermal evaporation. A longer deposition time of 60 min resulted in the formation of similar islands with modular grains on the pentacene thin film compared with 20 min and 30 min of deposition time. A comparison of the third-, fourth-, and fifth-order diffraction peaks revealed a higher diffraction intensity for pentacene thin film on ITO-coated glass and the presence of thin-film and bulk phases. Grain size and surface roughness increased as deposition time increased. The electrical characteristics of the metal/pentacene/metal structure revealed changes from the rectification to the ohmic behavior as the pentacene’s thickness increased. In addition, current density was influenced by the nature of the pentacene thin film. Thus, deposition time is an essential parameter in determining the molecular orientation and the electrical characteristics of pentacene for two-terminal device performance.

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REFERENCES

[1] N. Shioya, R. Murdey, K. Nakao, H. Yoshida, T. Koganezawa, K. Eda, T. Shimouka, and T. Hasegawa, “Alternative Face-on Thin Film Structure of Pentacene,” Sci. Rep., vol. 9, no. 1, pp. 1-7, 2019, doi: 10.1038/s41598-018-37166-6.
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[23] X. Zhang, M. Li, C. D. Agnese, G. Chen, X. Wang, and T. Miyasaka, “Thermo-evaporated pentacene and perylene as hole transport materials for perovskite solar cells,” *Dye and Pigment*, vol. 160, pp. 285-291, 2019, doi: 10.1016/j.dyepig.2018.07.053.

[24] M. Jang, S. K. Kim, J. Lee, S. Ji, W. Song, S. Myung, J. Lim, S. S. L ee, H. Jung, J. Lee, and K. An, “Amplifying gas sensor performance by embedding a cellulose-based buffer layer in organic transistors†,” *Journal of Materials Chemistry C*, pp. 21092–21099, 2019, doi: 10.1039/C9TC04889H.

[25] M. L. Mota, B. Rodriguez, A. Carrillo, R. C. Ambrosio, P. A. Luque, M. Mireles, I. Vivaldo, and M. A. Quevedo, “Fast and inexpensive synthesis of pentacene with high yield using 6, 13-pentacenequinone as precursor,” *J. Mol. Struct.*, vol. 1154, pp. 511–515, 2018, doi: 10.1016/j.molstruc.2017.10.070.

[26] D. K. Kim and S. Heutz, “Comparison of organic and inorganic layers for structural templating of pentacene thin films †,” *Materials Horizons*, 2019, doi: 10.1039/C9MH00355J.

[27] M. S. Mahdi, K. Ibrahim, A. Hmood, N. M. Ahmed, and A. Azzez, “A highly sensitive flexible SnS thin film photodetector in the ultraviolet to near infrared prepared by chemical bath deposition,” *RSC Advances*, pp. 114980–114988, 2016, doi: 10.1039/C6RA24491B.

[28] W. Khalidi, A. Boubaker, A. Nasri, K. Lnimouni, and A. Kalboussi, “Electrical study of pentacene-based metal-semiconductor-metal structure: Schottky barrier and active layer thickness effects,” *IEEE Trans. Electron Devices*, vol. 65, no. 11, pp. 5009–5013, 2018, doi: 10.1109/TED.2018.2869537.

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