



Letter

Tuning of the electrical characteristics of organic bistable devices by varying the deposition rate of Alq₃ thin film

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ABSTRACT

Organic bistable devices with an Al/Alq₃/n-type Si structure are investigated at different deposition rates of Alq₃ thin film. We can obtain current–voltage characteristics of these devices similar to those of metal/organic semiconductor/metal structures that are widely used for organic bistable devices. The bistable effect of the Al/Alq₃/n-type Si structure is primarily caused by the interface defects at the Al/Alq₃ junction. Moreover, the electrical properties of these devices can be modified and controlled by utilizing the appropriate deposition rates of the Alq₃ thin film by thermal deposition. XPS, AFM, and GIXRD measurements are performed to characterize the properties of Alq₃ thin film and Alq₃/Al interface. This type of devices involves an extremely simple fabrication process and offers great potential in future advanced organic electronics.

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1. Introduction

Due to advances in organic semiconductor materials, numerous organic conjugated materials have been extensively utilized in the production of electronic and optoelectronic devices [1–3]. Moreover, the demands for more accurate simulations in research and for consumer electronic devices are increasing dramatically. Along with this trend, a tremendous demand for increased memory capacity is also evident. In order to satisfy this current demand, the capacity of Si-based memory has been augmented by scaling down its size [4]. However, scaling down will reach its limit in the near future; therefore, organic-based memory [5–14] is one of the candidates of next generation

memory devices owing to the greater scope for better scalability offered by organic or polymeric mediums, low cost fabrication, and high mechanical flexibility. Therefore, potential memory devices based on polymeric or organic materials have attracted rapidly growing interest and are being widely investigated.

In this work, organic bistable devices with Al/tri-(8-hydroxyquinoline) aluminum (Alq₃) deposited on n-type Si substrate are fabricated and investigated. This device shows distinct bistability with an ON/OFF current ratio over 10⁶ and a wide reading voltage range for differentiating between “ON” and “OFF” states. The formation of the electrically bistable states is the result of electrons being trapped in the defects at the Schottky junction during electrical field stressing. This study also provides a simple approach, varying the deposition rate of the organic thin film, using which the characteristics of electrical bistability of the device, e.g., threshold voltage, can be tuned or controlled. XPS, AFM, and GIXRD measurements are performed to help us understand the properties of Alq₃

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thin film and Alq₃/Al interface and explain the experimental results obtained. Besides, the simple structure of the reported device indicates that it can be easily embedded into the well-developed semiconductor fabrication processes.

2. Experiments

The bistable device consists of an organic layer interposed between two electrodes. The fabrication process of the device is described as follows. First, a 150-nm-thick Alq₃ organic layer is deposited on a cleaned 1 Ωcm resistivity n-type silicon wafer by thermal deposition method in a vacuum below 3×10^{-6} Torr at room temperature. Then an 80-nm-thick aluminum top-electrode is deposited on the organic layer through a shadow mask. The size of each Al electrode is 0.64 mm². The deposition rates of the Alq₃ thin film are 0.05 nm/s, 0.15 nm/s, 0.2 nm/s, and 0.3 nm/s. The deposition rate is controlled by the setting temperature of the crucible and the corresponding setting temperature for each deposition rate is listed in Table 1. The current–voltage (*I*–*V*) characteristics are measured using a Hewlett Packard 4156A semiconductor parameter analyzer in an ambient environment. The capacitance–voltage (*C*–*V*) characteristics are recorded by an Agilent 4284A Precision LCR meter at a frequency of 1 MHz and amplitude of 25 mV. The surface morphology of the Alq₃ thin film on the Si wafer is obtained by using an atomic force microscope (AFM, DI-Veeco Instruments). The composition in the Alq₃/Al and the atomic concentration of the Alq₃ are analyzed using X-ray photoemission spectroscopy (XPS), while structural information is obtained via grazing incidence X-ray diffraction (GIXRD) analysis.

3. Results and discussion

Fig. 1 shows typical *I*–*V* characteristics of the fabricated Al/Alq₃/n-type Si structure. As can be seen, this device exhibits two different conductance states at an identical applied voltage. The silicon electrode is kept at 0 V, and all bias conditions are applied on the aluminum electrode. At the first bias (black curve in Fig. 1), the voltage sweeps from 0 V to 10 V. Initially, the device exhibits low conductance (OFF state). However, with an increased voltage, a transition from low conductance to high conductance (ON state) occurs at a threshold voltage of about 5 V, and then the device is maintained at a high conductance state. At the next bias (red curve in Fig. 1), the device still holds at high conductance. Therefore, this device possesses the nature of bistability. Furthermore, by applying a negative voltage from 0 V to –10 V, the device can be switched from

Table 1

Alq₃ thin film properties obtained from XPS measurements for different deposition rates of Alq₃ thin film under different setting temperatures

| Deposition rate (nm/s) | Setting temperature (°C) | N (atom%) | N/C |
|------------------------|--------------------------|-----------|-------|
| 0.05 | 251 | 6.8 | 0.075 |
| 0.15 | 267 | 6.2 | 0.068 |
| 0.2 | 274 | 6 | 0.066 |
| 0.3 | 281 | 5.9 | 0.065 |

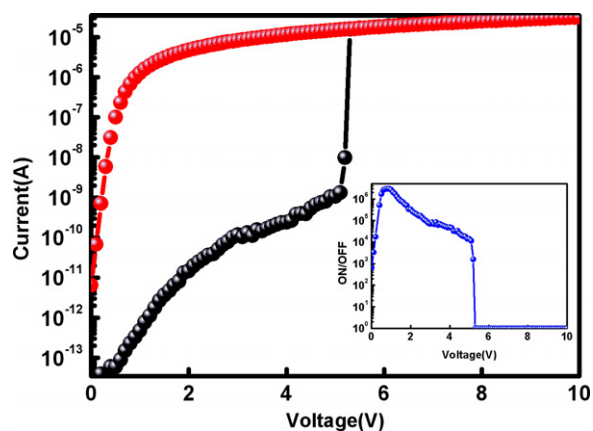


Fig. 1. Current–voltage characteristics of the fabricated device. The black and red curves represent writing and reading biases, respectively. The inset shows the voltage-dependent ON/OFF current ratio curve.

high conductance back to low conductance. The plot of ON/OFF current ratio as a function of reading voltage is shown in the inset of Fig. 1. It is obvious that the device has a very wide reading voltage range with large ON/OFF current ratio which may reduce reading errors and increase the reliability of the device. For this reason, the tolerance of this device is large enough for external surrounding circuitry to adopt. The corresponding reading currents after “writing” and “erasing” for the first four cycles are shown in Fig. 2.

At low bias of the first bias, the current is very small because electrons are obstructed by a barrier formed between the Si substrate and Alq₃. Thus, only a few electrons can be injected into the organic active layer. Then most of them are further trapped by the defects in the bulk Alq₃ thin film and at the interface of Schottky junction. As a result, the device stays at high resistance. By applying a voltage above the threshold, the barrier can be overcome, and this enables numerous electrons to be injected into the active layer and the defects can be filled. Accordingly, electrons are transported easily into the active layer and drift unobstructedly towards the other end of the device. At the next bias, the device exhibits a resistance-like

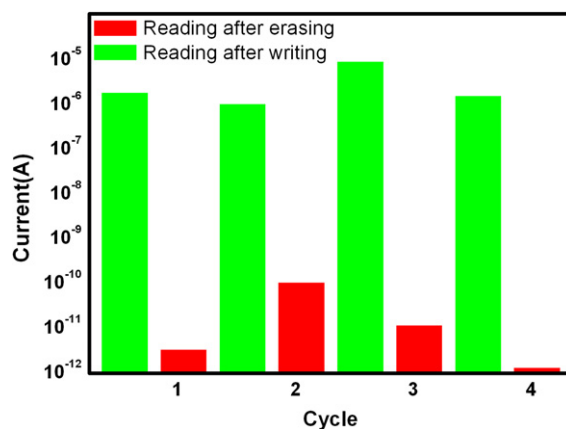


Fig. 2. The reading currents after “writing” and “erasing” of the reported device for the first four cycles.

characteristic when the reading voltage is larger than the energy barrier between Si and Alq₃, that is, ohmic relation. Thus, the ON state can be obtained for any reading voltage larger than the iso-type hetero-junction barrier between n-type silicon and Alq₃, which is about 0.65 eV from Fig. 1.

The bistable characteristic of the Al/Alq₃/n-type Si structure mainly originates from the defects at the interface of Schottky junction. Fig. 3 shows the C–V characteristic of the device. It can be seen from the curve that the device is kept at some capacitance value while the applied voltage is below the threshold. Then, the value changes into another lower capacitance value when the voltage exceeds its threshold. The variation of capacitance could be ascribed to the defects in the bulk Alq₃ thin film and at the interface of Schottky junction. At the initial stage of the applied voltage, few electrons are trapped by the defects in the low electrical field. Then, more and more electrons are trapped by the defects as the voltage increases. While the applied voltage is near the threshold, defects are filled sufficiently to make the device possess a metal-like property; consequently, the capacitance is converted

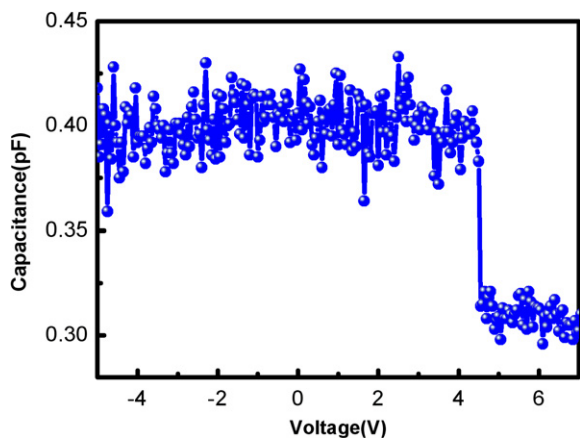


Fig. 3. Capacitance–voltage characteristic of the device at a frequency of 1 MHz. The Si electrode is kept at 0 V, and the voltage on the Al electrode is swept from –5 V to 7 V.

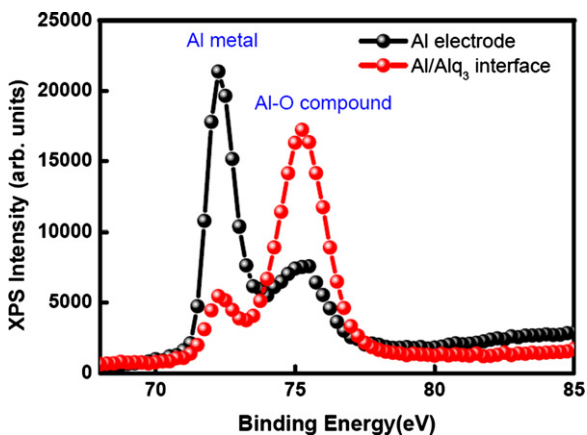


Fig. 4. XPS curves of Al electrode and Al/Alq₃ interface of our reported device.

into a lower value. In addition, the *I*–*V* curve of the Al/Alq₃/n-type Si structure with one small Al drop as the top electrode does not exhibit bistability but rather diode behavior. This indicates that the interface property between Al electrode and Alq₃ thin film plays an important role for bistability. A significant chemical reaction occurs

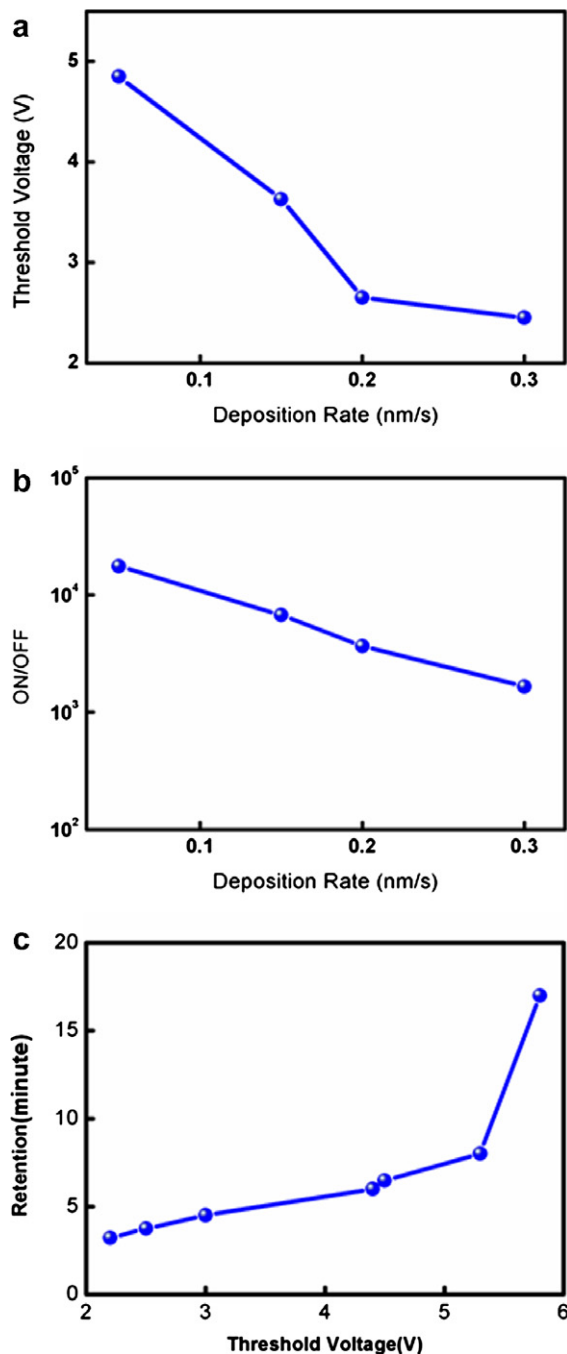


Fig. 5. Electrical properties of the device with different deposition rates of the Alq₃ thin film: (a) deposition-rate dependent threshold voltage, (b) deposition-rate dependent ON/OFF current ratio, and (c) threshold-voltage dependent retention time. Data points shown in (a) and (b) are average values measured from our fabricated devices.

at the interface when aluminum is thermally deposited on the Alq₃ thin film [15]. The resulting product, supportively consisting of Al–O interactions, serves as interface traps and makes carriers be poorly injected through the Schottky junction interface. For this reason, trapping charges at the interface between Alq₃ and Al primarily control the switching mechanism. Fig. 4 shows the XPS curves of the Al electrode and the Alq₃/Al interface of the reported device, which clearly confirms the existence of Al–O compound at the Alq₃/Al interface.

The electrical behavior of the device can be modified by varying the deposition rate of the organic active layer. Fig. 5a and b shows the deposition rate effect on the threshold voltage and ON/OFF current ratio of the device: both decrease with an increase in the deposition rate of Alq₃ thin film. In addition, as can be seen in Fig. 5c, the retention time is dependent on the threshold voltage of the device. Since the threshold voltage can be tuned by adjusting the deposition rate of the organic thin film, the retention time can be extended by reducing the deposition rate of the organic thin film.

Previous reports on the morphology of the organic thin film indicate that roughness decreases with the deposition rate [16,17]. That is to say, the effective surface area between Alq₃ and Al can be adjusted by regulating the deposition rate of Alq₃. For that reason, a higher deposition rate introduces a relatively small amount of defects at the

Schottky junction interface. Fig. 6 shows the AFM images of the Alq₃ thin films deposited at 0.05 nm/s, 0.15 nm/s, 0.2 nm/s, and 0.3 nm/s, respectively. The corresponding surface roughness means are 0.38 nm, 0.35 nm, 0.31 nm, and 0.17 nm. These reveal that the deposition rate of the Alq₃ thin film is a major factor in the adjustment of effective contact surface area between Alq₃ and Al. Effective contact surface area will affect the amount of the interface defects of the device. As a result, the relative amount of the defects at the Schottky junction interface can be modified by controlling the deposition rate of the organic thin film. Furthermore, Fig. 7 shows grazing incidence X-ray diffraction curves of the Alq₃ thin film deposited at different rates. It is obvious that all Alq₃ thin films are with amorphous diffraction patterns. In other words, crystallization does not occur in all organic thin films. That is, threshold voltage, ON/OFF current ratio, and retention time are not related to crystallization quality of thin film. They are closely related to the film roughness, as shown by the AFM images in Fig. 6. Besides, it has been demonstrated that the atomic N/C ratio of the Alq₃ thin film changes with the deposition rate of the Alq₃ thin film [16,17]. At a higher deposition rate, that is, higher temperature condition, the Alq₃ molecule structure disintegrates to release N-containing species due to the decomposition energy of Alq₃ being smaller than its sublimation energy. It is also shown that the Alq₃ thin film deposited at a lower deposition rate

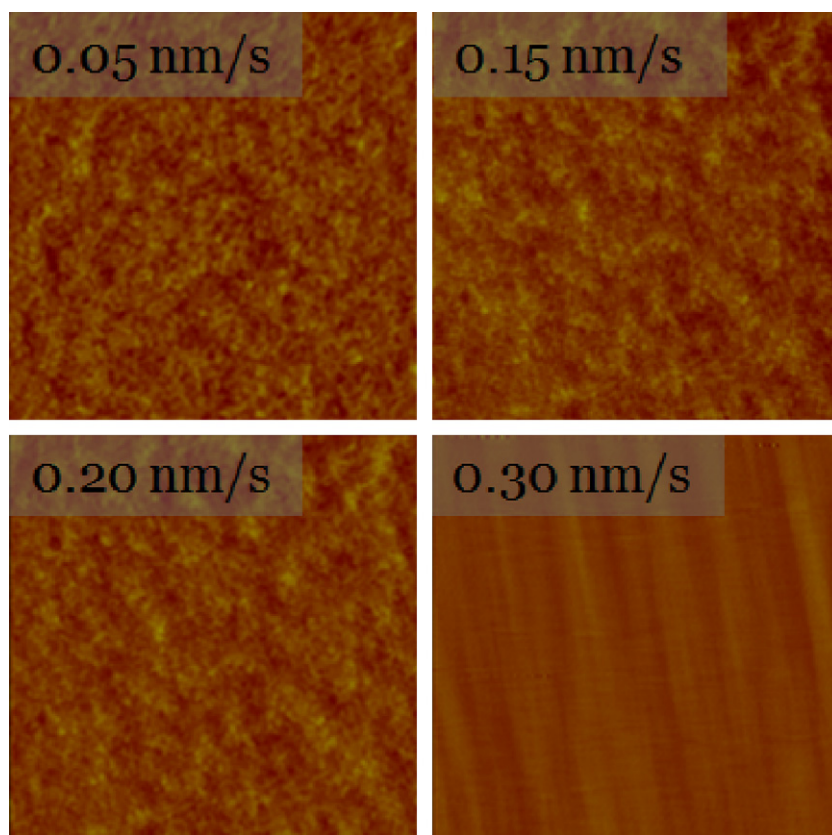


Fig. 6. AFM images of the Alq₃ thin film deposited on n-type Si wafer at four different deposition rates. Surface roughness means are 0.38 nm, 0.35 nm, 0.31 nm, and 0.17 nm for deposition rates at 0.05 nm/s, 0.15 nm/s, 0.2 nm/s, and 0.3 nm/s, respectively.

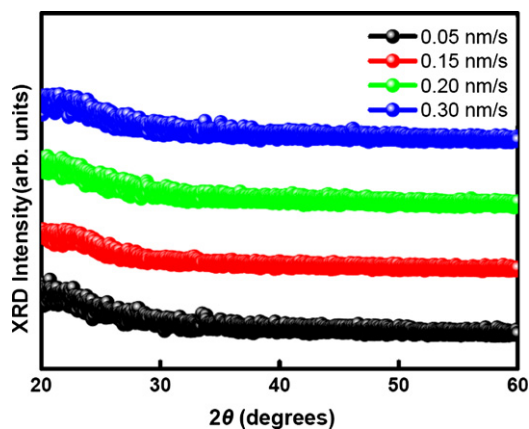


Fig. 7. Grating incidence X-ray diffraction (GIXRD) curves of the Alq₃ thin films for different deposition rates.

contains a greater atomic concentration of nitrogen and a higher atomic *N/C* ratio. The corresponding concentrations of *N* and atomic *N/C* ratios from XPS measurements for different deposition rates of Alq₃ thin film are given in Table 1, which clearly indicates the same trend discussed above. Moreover, the electrons being injected into the Alq₃ thin film undergo a repulsive force generated by the negatively charged nitrogen atoms which is the result of the electronegativity of a nitrogen atom being larger than that of a carbon or oxygen atom for a neutral Alq₃ molecule [18]. Hence, the electrons in the Alq₃ thin film with smaller *N/C* ratio experience less repulsive force [17]. In other words, an increase in the deposition rate of the Alq₃ thin film can extend the hopping distance and raise hopping frequency of electrons in the Alq₃ thin film.

From above discussions, two findings can be made to explain the results obtained in Fig. 5a and b. First, it is obvious that threshold voltage decreases with increasing deposition rate because of a smaller amount of defects at the Schottky junction interface at a higher deposition rate. Second, the same relationship for the ON/OFF current ratio is because a smaller amount of nitrogen atoms are available to prevent the electrons from hopping in the Alq₃ thin film, hence increase the low conductance state current and decrease the ON/OFF current ratio at a higher deposition rate. Additionally, the distribution of defects at the interface corresponds to the trapping energy [19]. These defects can be classified roughly into two groups: low trapping energy defects (E_{low}) and high trapping energy defects (E_{high}). Higher deposition rate of Alq₃ thin film introduces smoother Alq₃ surface roughness, and may produce less E_{high} . A sample with a smaller threshold voltage, resulting from higher deposition rate and smaller surface roughness of Alq₃, exhibits shorter retention time probably due to less E_{high} . The trapped electrons are more easily released from the E_{low} defects at the Schottky junction interface. Therefore, the electrons can not be kept longer in the E_{low} defects

and the device has shorter retention time, as shown in Fig. 5c. Consequently, the deposition rate of Alq₃ thin film has a significant effect on the electrical properties of the organic bistable devices, e.g., threshold voltage, ON/OFF current ratio, and retention time. The electrical characteristics of the device can be optimized and tuned according to our needs for different situations based on the trends obtained in these experiments. Of course some tradeoffs must be made.

4. Conclusions

In summary, the current–voltage characteristics of the organic bistable device, Al/Alq₃/n-type Si, are investigated. This bistability results from the interface defects at the Alq₃/Al junction. Promising results for thermal deposition with controllable film quality by varying the deposition rate of Alq₃ thin film are also provided. The properties of Alq₃ thin film and Alq₃/Al interface are obtained by XPS, AFM, and GIXRD measurements. Owing to the simple structure of the device, the organic electronic memory device can be embedded into the conventional silicon-based fabrication processes. Furthermore, this device has great potential for high-density data storage, low-cost memory applications in future nanoelectronics.

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