

## Experimental observation of oxygen-related defect state in pentacene thin films

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The authors report on a metastable defect observed in pentacene thin films. The defect, which is characterized by a hole trap at  $E_v+0.6$  eV and attempt-to-escape frequency of  $5 \times 10^{12} \text{ s}^{-1}$ , can be reversibly created/removed under a negative/positive bias voltage applied to the aluminum/pentacene Schottky diode at room temperature in air. Annealing the sample in vacuum at 360 K removes the defect and prevents its creation by application of any bias voltage in vacuum. Considering recent calculations of defects in pentacene the authors assume that the defect is formed by replacing one of the hydrogen atoms by an oxygen atom ( $\text{C}_{22}\text{H}_{13}\text{O}$ ). © 2007 American Institute of Physics. [DOI: 10.1063/1.2710203]

Several papers have recently reported on metastability of electronic properties of pentacene crystals,<sup>1,2</sup> thin films,<sup>3</sup> and organic thin film transistors<sup>4</sup> (TFTs) due to bias stress or air exposure effects. Nevertheless, there is lack of experimental data which are essential for identification of defects and successive elimination of their deleterious effects on device performance. So far TFT structures were employed as a main tool for investigating the physical properties of pentacene.<sup>4-6</sup> Only a few papers report on pentacene characterization by other techniques, such as deep defect states in the metal/insulator/organic semiconductor structure investigated by capacitance deep-level transient spectroscopy<sup>7</sup> (DLTS) or the recently described defect generation and quenching by bias stress observed in space-charge limited current.<sup>2</sup> Charge DLTS has been utilized to study the defect states in undoped hydrogenated amorphous silicon.<sup>8,9</sup> Since charge (current) DLTS can benefit from direct detection of released charge from deep states, there is no need to detect capacitance changes of depletion layer.

In this letter, we will report on metastable oxygen-related defect state in pentacene thin film detected with charge DLTS. We observed a defect state with activation energy of 0.6 eV that can be reversibly created/removed under a negative/positive bias voltage applied in air to the Schottky barrier. This metastable state cannot be induced with any bias treatment after annealing the sample at 360 K in vacuum and keeping it there. Taking into account previous calculations<sup>1</sup> and experimental data<sup>2,10,11</sup> a possible origin of this defect state in pentacene thin film is discussed.

Pentacene thin films were deposited on  $p^+ c$ -Si substrate by thermal evaporation in a high-vacuum chamber with the

base pressure of  $10^{-6}$  mbar.<sup>12,13</sup> The pentacene source is commercially available from Aldrich Chemical (98% pure) and no further purification steps were performed. The pentacene films were grown at moderate deposition rates ( $<10 \text{ Å/s}$ ) at three different substrate temperatures of 303, 333, and 363 K. The thickness of the studied samples was around 800 nm. The microstructure of the pentacene thin films evidences the coexistence of thin film and bulk triclinic crystalline phases. Schottky-type contacts were deposited on pentacene by thermal evaporation of aluminum through a shadow metallic mask with an area of  $1 \times 1 \text{ mm}^2$ .

The pentacene samples were investigated with a time domain spectrometer where capacitance vs voltage ( $C$ - $V$ ) and the charge DLTS techniques are implemented.<sup>14</sup> The isothermal mode of charge DLTS measurements was used, i.e., the sampling events  $t_1$ ,  $2t_1$ , and  $4t_1$  were swept ( $t_1$  from 2  $\mu\text{s}$  to 10 ms, 19 points per decade) instead of temperature sweep used in the standard DLTS. The isothermal mode prevents the properties of organic semiconductors from changing with temperature and thus more reliably evaluates parameters of the investigated defect states. Since undoped pentacene layer is nominally slightly  $p$ -type semiconductor reverse bias  $U_b=3$  V with excitation pulses  $\Delta U=-3$  V was applied to the gate electrode in order to detect any relaxation due to hole emission from deep states. Using the set of spectra recorded at several temperatures from 240 to 360 K activation energies of the measured DLTS peaks were determined from Arrhenius plots.

$C$ - $V$  curves give capacitance above 30 pF at positive voltages (reverse bias) and the capacitance slightly increases to around 35 pF for negative voltages (forward bias). Unlike standard Schottky barrier, there is no steep increase of the capacitance for voltages close to zero. This effect can be due

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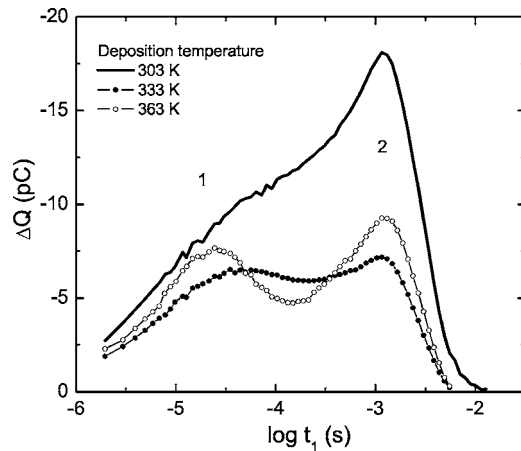


FIG. 1. Isothermal charge DLTS spectra of the pentacene thin films as deposited, prepared at three different substrate temperatures. Measurements were performed with reverse bias  $U_b=3$  V and excitation pulses  $\Delta U=-3$  V at room temperature in air.

to the insufficient concentration of free carriers which could respond within the interval of the used sampling time of 10 ms. This sampling time corresponds approximately to a frequency of 100 Hz.

Two isothermal charge DLTS peaks are recognized in as-deposited pentacene thin films for all three substrate temperature depositions (Fig. 1). Peak 1 is located at around 10  $\mu$ s and peak 2 at around 1 ms. Generally, besides the emission process from deep levels, charge transients can be caused by dielectric polarization or discharging of the sample capacitance. It is possible to identify these processes by the application of excitation pulses of opposite polarity. Regarding the emission from deep levels no signal is to be observed in such condition. As it can be seen in Fig. 2, peak 1 is also measured for opposite polarity of pulses. It indicates that the corresponding relaxation is not due to emission from a deep level. If we consider the capacitance of the measured sample and the resistance of the pentacene thin film,<sup>12,13</sup> we get a time constant for discharging RC element which is in accordance with the measured value of 10  $\mu$ s. The activation energy and the attempt-to-escape frequency of this relaxation are 0.31 eV and  $4 \times 10^{10}$  s<sup>-1</sup>, respectively. The former value is very close to the activation energy of conductivity for

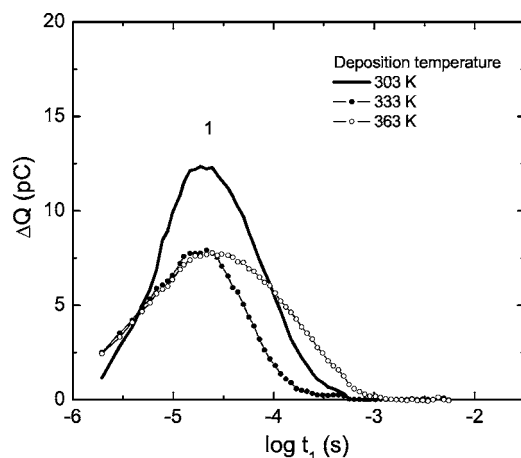


FIG. 2. Isothermal charge DLTS spectra of the pentacene thin films as deposited, prepared at three different substrate temperatures. Measurements were performed with reverse bias  $U_b=0$  V and excitation pulses  $\Delta U=+3$  V at room temperature in air.

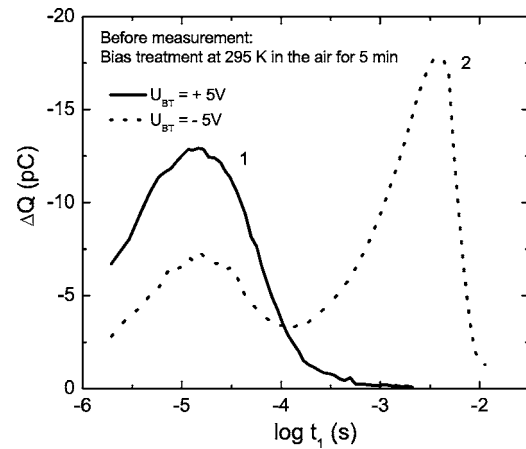


FIG. 3. Effect of the bias treatment on isothermal charge DLTS spectra of the pentacene thin film deposited at 303 K. Before measurements the sample was kept at room temperature and at +5 V (full line) or -5 V (dotted line) for 5 min in air. Measurements were performed with reverse bias  $U_b=3$  V and excitation pulses  $\Delta U=-3$  V at room temperature in air.

undoped pentacene thin film under investigation.<sup>12</sup> Peak 2 is observed only for the negative polarity of pulses ( $\Delta U=-3$  V) which corresponds to filling pulses for holes and it has all the attributes of an emission process from a deep level. This peak diminishes with decreasing the measuring bias voltage which indicates a bulk related level. We have found that the defect corresponding to peak 2 is sensitive to the bias voltage applied before the measurement and exhibits metastable behavior. Peak 2 is completely removed with a bias voltage of +5 V applied to the gate for 5 min before measurement (see Fig. 3) while peak 1 remains after this bias treatment. The bias voltage of -5 V applied in air for 5 min before measurement (see Fig. 3) restores peak 2. Contrary to the situation in the as-deposited state peak 2 after the latter bias treatment is located at around 4 ms and is well defined for pentacene thin films deposited for all three substrate temperatures. It should be noted that both states of the pentacene thin films prepared at opposite bias voltages ( $U_b=-5$  V, +5 V) are metastable. After keeping the samples without any bias at room temperature for more than 1 h, DLTS measurements yield spectra similar to as-deposited states, which is demonstrated in Fig. 4 for thin film prepared at 363 K. Metastable states can be reintroduced by repeated application of a particular bias voltage. Depending on the Fermi-level position which is changed by the application of the bias voltage from -5 to +5 V, the amplitude of peak 2 gradually decreases and shifts to shorter relaxation times. Considering the above-mentioned behavior it is conceivable that the defect associated with peak 2 has several metastable configurations and completely disappears for the bias voltage of +5 V. Recording charge DLTS spectra at several temperatures for a sample subjected to bias treatment at -5 V in the air before measurement at each temperature, the activation energy and the attempt-to-escape frequency of peak 2 were determined to be 0.6 eV and  $5 \times 10^{12}$  s<sup>-1</sup>, respectively. The higher the deposition temperature, the smaller the amplitude of peak 2, which is proportional to the concentration of the defect. To examine the role of oxygen for the observed metastable defect, our sample was annealed at 360 K for 5 min in rotary pump vacuum of 50 Pa. Charge DLTS spectra after such a treatment (the measurements are also made under vacuum) give only peak 1 and peak 2 is removed. Peak 2

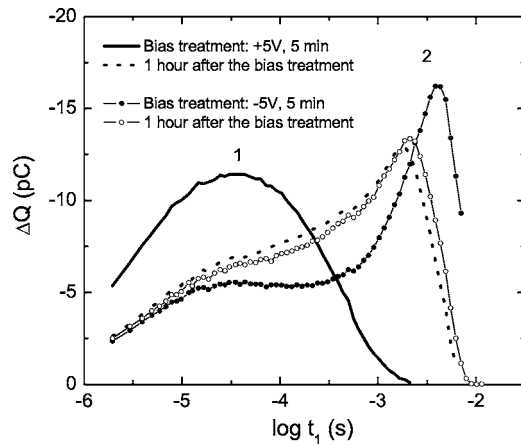


FIG. 4. Metastable behavior of pentacene thin film. After keeping the samples without any bias at room temperature for 1 h DLTS measurements yield spectra similar to as-deposited states regardless of the previous bias treatment (bias voltage +5 or -5 V). The deposition temperature of the pentacene thin film is 363 K.

cannot be reintroduced regardless of any bias treatment performed in vacuum and it is only observed after repeated exposure of the sample to air.

Several papers reported on the acceptorlike states that are caused by oxygen and/or moisture.<sup>10,11,15</sup> It was shown by thermogravimetric analysis that pure O<sub>2</sub>, N<sub>2</sub>, and Ar can be reversibly incorporated in the pentacene crystal.<sup>10</sup> Fitting the time evolution of the molar fraction of dry air in pentacene yields the diffusion coefficient of 10<sup>-10</sup> cm<sup>2</sup> s<sup>-1</sup> for molecules of air at room temperature. Unlike the exposure to pure N<sub>2</sub> and Ar, which causes insignificant changes in the electrical properties, incorporated oxygen increases hole conduction. Further *in situ* electrical measurements prove that oxygen is incorporated in the pentacene polycrystalline film by exposing the sample to atmosphere.<sup>11</sup> These measurements reveal strong influence of the morphology of the film on the TFT stability. The influence of oxygen on the device operation is reduced with increasing size of the pentacene crystals. It was also reported that the pentacene TFT can be utilized as humidity sensor.<sup>15</sup> The one order drop in the source-drain current after exposure to humidity was attributed to the decrease of the hole mobility. This effect was very small (less than 5%) in O<sub>2</sub> and CO<sub>2</sub> atmosphere and practically no change was observed in N<sub>2</sub> atmosphere. Effect of the bias-stress generation and quenching of defects in pentacene was recently observed in single crystals by Lang *et al.*<sup>2</sup> When the bias stress was applied hole trap with a mean activation energy of 0.38 eV was detected in space-charge limited current curves. Without applied bias voltage this trap disappeared at room temperature in the dark for more than 1 h. Since the activation energy of the hole trap was very similar to the energy (0.34 eV) of a defect formed by adding a H atom to the pentacene molecule, which was calculated by Northrup and Chabinye,<sup>1</sup> this trap was associated with C-H<sub>2</sub> defect.

Considering the diffusion coefficient of 10<sup>-10</sup> cm<sup>2</sup> s<sup>-1</sup> in pentacene at room temperature<sup>10</sup> the diffusion length of air molecules for annealing conditions (360 K, 5 min) is longer than the thickness of our thin films. We assume that these molecules diffuse out of the bulk along the edges of Al electrodes during annealing in vacuum. The reversible appearance of peak 2 detected in our polycrystalline samples therefore indicates that oxygen and/or moisture should be involved in the corresponding defect. The determined activation energy and the bias-voltage condition for its observation are in accordance with the parameters of defect, formed by replacing one of the H atoms by an oxygen atom (C<sub>22</sub>H<sub>13</sub>O), which was calculated by Northrup and Chabinye.<sup>1</sup>

In summary, a metastable defect was observed in pentacene thin films. The associated deep level is characterized by an activation energy and attempt-to-escape frequency of 0.6 eV and 5 × 10<sup>12</sup> s<sup>-1</sup>, respectively. The defect can be reversibly created/removed under a negative/positive bias voltage applied to the aluminum/pentacene Schottky diode at room temperature in air. Also, annealing the sample in vacuum at 360 K removes the defect and prevents the creation of this defect by application of any bias voltage in vacuum. We assume that the above-mentioned defect is formed by replacing one of the hydrogen atoms by an oxygen atom.

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