



## Organization of Pentacene Molecules on Anisotropic Ultrathin HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Templates for Organic Thin-Film Transistors Using an Ion-Beam Treatment

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This article investigates improving organic thin-film transistor (OTFT) characteristics by using an alignable high dielectric constant film to control the self-organization of pentacene molecules. The process, based on the growth of a pentacene film with high vacuum sublimation, is a method of self-organization that uses ion-beam (IB) bombardment of the HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> surface that serves as the gate dielectric layer. X-ray photoelectron spectroscopy indicates that the IB increases the structural anisotropy of the HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> film, and X-ray diffraction patterns show that increasing the anisotropy may lead to the self-organization of pentacene molecules in the first polarized monolayer. An effective mobility of  $2.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was achieved, which is significantly different from the mobility in pentacene films that are not aligned. The proposed OTFT devices with an ultrathin HfO<sub>2</sub> structure as the gate dielectric layer were operated at a gate voltage lower than 5 V.

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The performance of organic thin-film transistors (OTFTs), as characterized by such parameters as field-effect mobility, modulated on/off current ratio, and threshold voltage, depends in part on the molecular structure of the semiconducting film. Thus several studies focused on improving the performance of pentacene-based thin-film transistors (TFTs) have sought to optimize growth conditions, such as deposition rate, roughness, and the surface treatment. In particular, recent attempts to improve the field-effect mobility in pentacene-based TFTs have involved pentacene-ordering methods.<sup>1-5</sup> The carrier mobility in an OTFT should be enhanced if the pentacene molecules can be aligned so as to increase the  $\pi$ -orbital overlap along the direction of current flow. Therefore methods such as friction transfer, rubbing, photoalignment, and imprinting lithography have been developed to fabricate an aligned layer. These methods all have certain limitations, however, such as requiring a supplemental photoalignment layer and being complicated processes that require high voltages for their operation.

To solve these problems, this article introduces a process of ion-beam (IB)-induced pentacene alignment on ultrathin HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> double layers. To obtain a high quality alignment layer, we grow HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> layers by atomic layer deposition (ALD), which has the advantages of excellent control of layer thickness as well as good conformity and uniformity.<sup>6-9</sup> This added buffer layer forms a HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> dielectric structure, which reduces the negative effects of the bottom interface, such as excessive leakage current or poor gate dielectric reliability. This has an effect not only on the control of the threshold voltage but also on the electronic structure of the interface between the dielectric layers and the organic semiconductor. Experimental results indicate that using the IB-treated high-*k* multilayers results in good device performance, low driving voltages, and enhanced field-effect mobilities.

### Experimental

An IB-treated HfO<sub>2</sub> surface was used as an alignment layer to control the orientation of the pentacene molecules, thus producing films with strong anisotropic field-effect mobilities. We began by using ALD to deposit a 10 nm thick Al<sub>2</sub>O<sub>3</sub> thin film on a glass substrate using trimethylaluminum [Al(CH<sub>3</sub>)<sub>3</sub>] (TMA) and water at a deposition temperature of 300°C. We controlled the Al<sub>2</sub>O<sub>3</sub> film thickness by varying the number of deposition cycles, where each

deposition cycle consisted of a water pulse, a nitrogen purge, a TMA pulse, and a nitrogen purge. This Al<sub>2</sub>O<sub>3</sub> layer served as a barrier layer to prevent interface charge trapping and leakage. A 10 nm thick HfO<sub>2</sub> thin film was fabricated with ALD, using HfCl<sub>4</sub> and water as precursors at a deposition temperature of 300°C, to serve as the pentacene alignment layer.

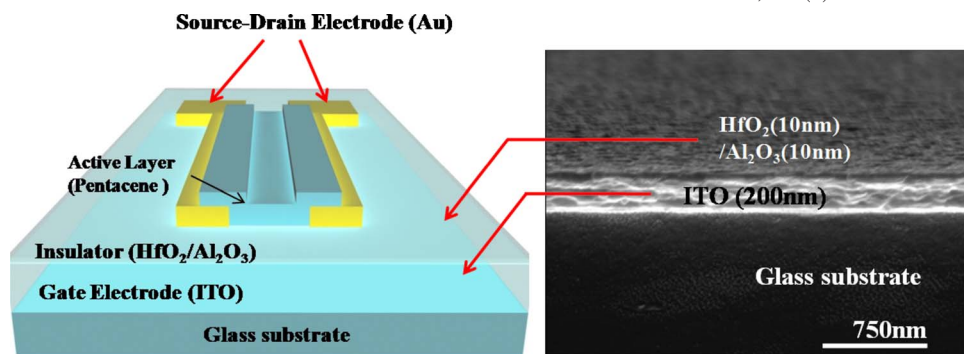
After creating this 20 nm thick, high dielectric HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> layer, we irradiated the HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> surface with an argon-ion beam having an energy of 2400 eV at an incident angle of 45° to the plane of the substrate.<sup>7,10,11</sup> We previously reported that the beam's effect on the alignment depends on the energy and time of the IB irradiation.<sup>10,11</sup> Thus lower energies of irradiation and smaller incident angles produce poorly oriented pentacene films.<sup>2,10,11</sup> After the irradiation, a gold gate electrode was deposited. Then, as illustrated in Fig. 1, we deposited a 70 nm thick pentacene film with a thermal evaporator (DOV Co. Ltd.), and a bottom-gate TFT device with pentacene was fabricated on top of the HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The width and length of the channel were 1500 and 100  $\mu\text{m}$ , respectively.<sup>12</sup>

### Results and Discussion

We used X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and atomic force microscopy (AFM) to investigate the chemical and physical mechanisms of the intermolecular chemical reaction between the HfO<sub>2</sub> and the pentacene caused by the IB irradiation. Figure 2a and b shows the XPS spectra for O 1s before and after the IB exposure. The spectra have subpeaks centered at 529.6 and 531.3 eV which represent, respectively, the O-Hf and O-Al bonds. The IB irradiation caused significant changes in the intensities of the O 1s spectra; in particular, the intensity in the signal from the O-Hf bonds has decreased. This change in intensity is apparently due to the anisotropic formation at the HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> surfaces.<sup>7,8</sup> The orientation of the pentacene molecules is affected by this anisotropy when they are deposited on the Hf-O<sup>-</sup> surface as it interacts strongly with pentacene. This result suggests that IB irradiation could allow for the direct chemical bonding of the activated Hf-O<sup>-</sup> to the pentacene. The presence of such bonding is also supported by FTIR spectroscopy of the pentacene (Fig. 2c). Furthermore, the IR absorption in the 908 cm<sup>-1</sup> region is due to the properties of pentacene.<sup>5</sup> The change in the shape of the IR spectra between the 955 and the 908 cm<sup>-1</sup> region suggests that the IB irradiation produces structural changes in the interfacial reaction that allow the reactive oxygen atoms on the HfO<sub>2</sub> surface to combine preferentially with the pentacene.<sup>13</sup> The two bands at 908 and 955 cm<sup>-1</sup> are assigned to the

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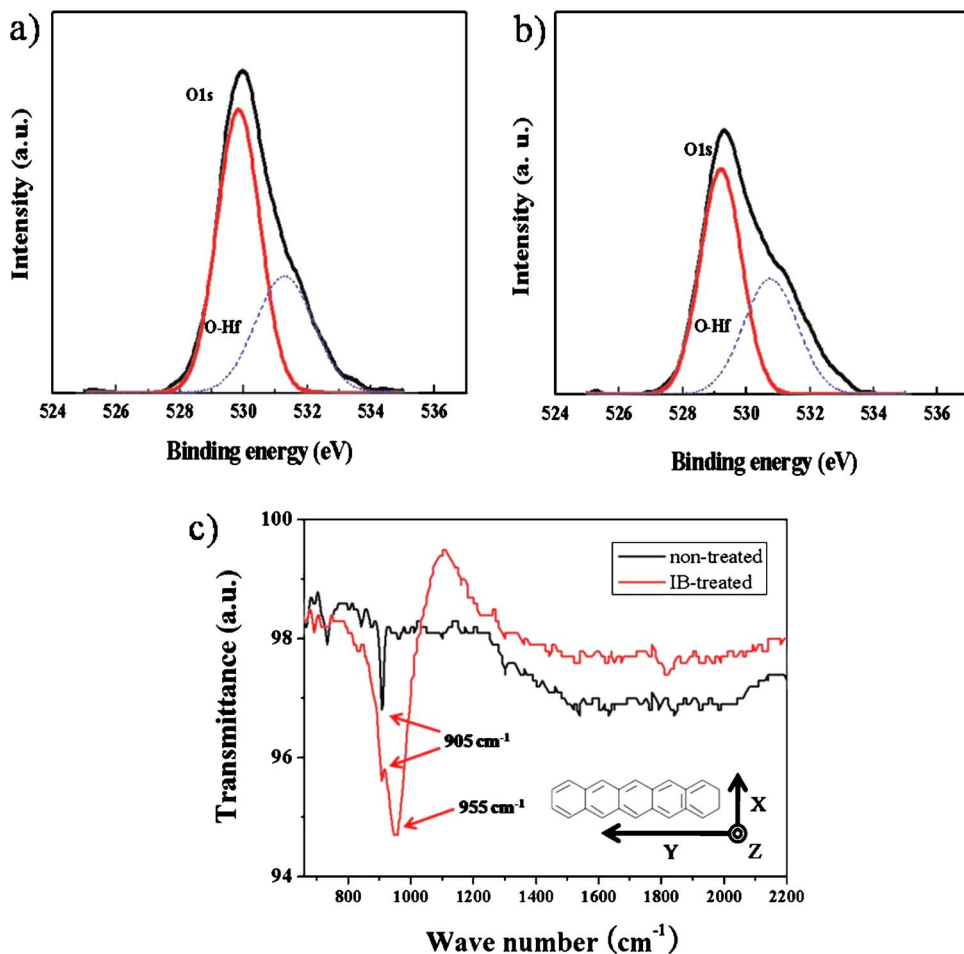
**Figure 1.** (Color online) Schematic of the three-dimensional structure of the bottom-contact electrode device and a scanning electron microscopy image of the 20 nm thick  $\text{HfO}_2/\text{Al}_2\text{O}_3$  layer on the ITO surface.

C–H out-of-plane bending vibrations polarized along the  $z$  axis.<sup>5</sup> These results imply that optimal  $\pi$ -orbital overlap in a pentacene film can be obtained along the orienting direction which, in turn, enhances the field-effect mobility.<sup>1-3,14</sup>

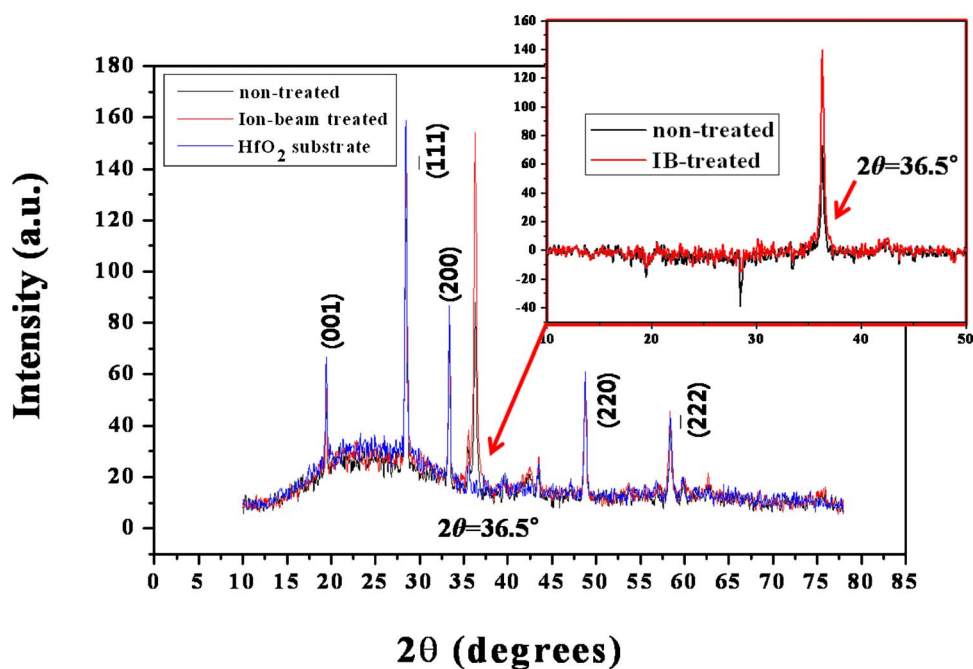
In characterizing the thin-film characteristics, we used XRD (Rigaku) to study the crystallinity of the films; the results are shown in Fig. 3. The  $\text{HfO}_2/\text{Al}_2\text{O}_3$  characteristics are generally reflected in the shape of the (111), (200), and (220) peak patterns, which matched the JCPDS (card no. 34-0104) database closely.<sup>4</sup> The peak near  $2\theta = 36.5^\circ$  (see magnified inset in Fig. 3) clearly corresponds to the oriented pentacene layer, whose crystalline phases are increased after the IB irradiation. Figure 4a and b shows the morphologies of the pentacene film on the IB aligned and the nontreated  $\text{HfO}_2/\text{Al}_2\text{O}_3$  films, respectively. Generally speaking, the wave-shaped islands are aligned parallel to the direction of the  $\text{HfO}_2/\text{Al}_2\text{O}_3$  alignment, and they are present on top of the oriented grains of the IB-aligned  $\text{HfO}_2/\text{Al}_2\text{O}_3$  surface; by contrast, on the

nontreated  $\text{HfO}_2/\text{Al}_2\text{O}_3$  surface, these islands are rarely seen, and they are arranged irregularly. Both the increased orientation and the elongation of the grains indicate that the alignment of the  $\text{HfO}_2/\text{Al}_2\text{O}_3$  surface significantly affected the growth of the pentacene film.

Figure 5 shows the drain current plotted against the gate-source voltage for three different devices at a fixed value of the drain-source voltage. The lines represent the data from the device with the pentacene layer oriented parallel to and perpendicular to the direction of the current flow in the channel as well as from a reference device with an unaligned surface. All of these devices demonstrated desirable TFT characteristics with operating voltages of less than  $-5$  V. When the orientation of the pentacene is parallel to the direction of the current flow, the maximum saturation current is  $0.9 \mu\text{A}$  compared to  $0.4 \mu\text{A}$  when the orientation of the pentacene is perpendicular to the direction of the current flow. The field-effect mobility for devices fabricated on the unaligned surface was 1.1



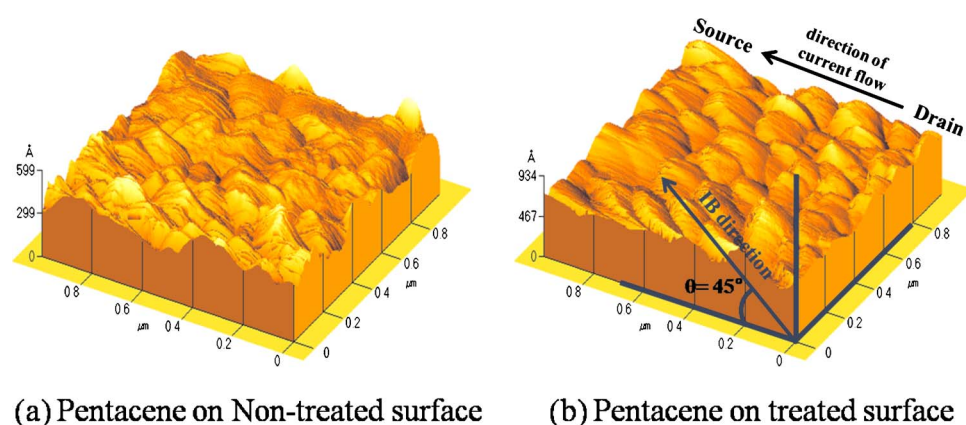
**Figure 2.** (Color online) Curve fitting of the XPS spectra for the O 1s peaks from the  $\text{HfO}_2$  thin films and IR spectra of the pentacene film: (a) before IB treatment and (b) after IB treatment at 2400 eV. These results show the intensity of the  $\text{HfO}_2$  O 1s peaks as a function of the IB treatment. (c) IR spectra of the pentacene film deposited on top of the nontreated and IB-treated  $\text{HfO}_2$ : Two bands at 908 and  $955 \text{ cm}^{-1}$  are assigned to the polarized pentacene along the  $z$  axis.



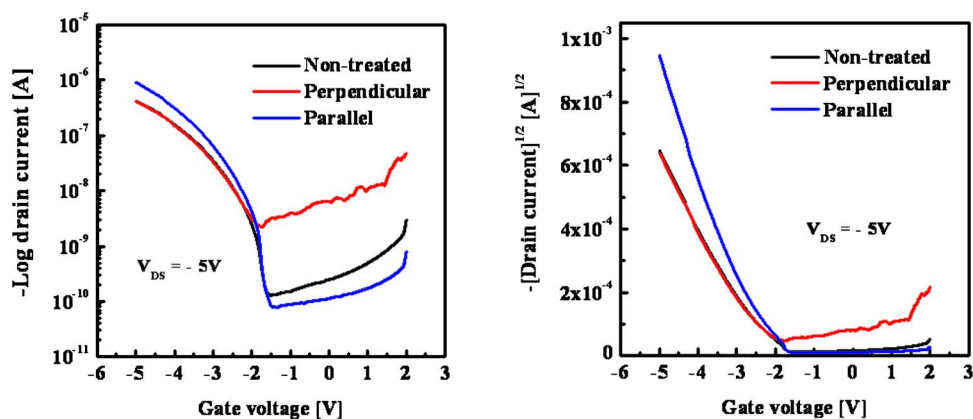
**Figure 3.** (Color online) XRD spectra of the pentacene film on the ALD  $\text{HfO}_2$  substrate. The increase in intensity of the peak at  $2\theta = 36.5^\circ$  indicates an enhancement of the crystallinity after the IB treatment.

$\times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . When the direction was oriented parallel to the direction of the current flow, the device exhibited an improvement in its field-effect mobility relative to that of the control sample. Furthermore, the field-effect mobility in the parallel direction was higher than that obtained in the perpendicular direction. The mobility, calculated in the saturation regime, was  $2.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the parallel alignment and only  $9.6$

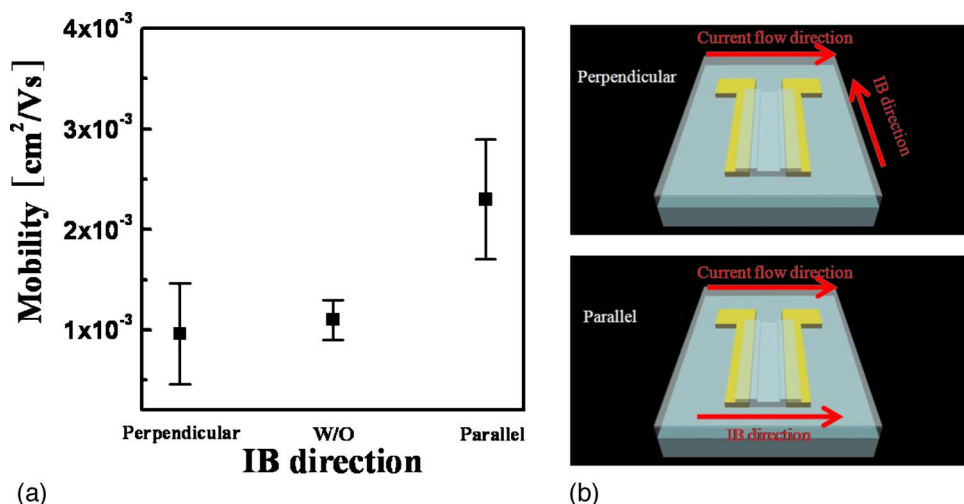
$\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the perpendicular case, yielding a mobility anisotropy ratio greater than 2 (Fig. 6). Furthermore, OTFTs treated in the parallel direction give better performance for the threshold voltage, the off currents, the current on/off ratios, and the subthreshold swings than the other devices, both the OTFTs treated in the perpendicular direction and those without treatment. The mobility anisotropy and enhancement can be attributed to the increased



**Figure 4.** (Color online) (a) AFM images of the pentacene film on nontreated  $\text{HfO}_2$ . (b) AFM images of the pentacene film on the IB-aligned  $\text{HfO}_2$  surface. The orientation of the pentacene is parallel to the IB alignment direction on  $\text{HfO}_2$ .



**Figure 5.** (Color online) Current-voltage characteristics of an OTFT. (a)  $\log I_D$ . (b) Square root of the drain current ( $\sqrt{I_D}$ ) as a function of  $V_G$  (from +2 to -5 V) at the drain to source voltage ( $V_{DS} = -5 \text{ V}$ ). Each of the lines represents data from the reference device with the nontreated and IB-treated layers.



**Figure 6.** (Color online) (a) The mobility in the cases of IB-treated parallel alignment, an unaligned surface, and perpendicular alignment. (b) The electrode configurations when the direction of IB irradiation was aligned perpendicular to and parallel to the direction of current flow, respectively.

tilted orientation of the pentacene moieties, as shown in Fig. 4b. Nonuniform grains with a tilted orientation would present significant boundary effects and result in increased charge trapping in the pentacene layer. Therefore, the preferential orientation and the elongation of the grains are both responsible for not only the anisotropy but also the enhancement of the field-effect mobility. Table I summarizes the parameters for all the proposed devices. The results are based on pentacene deposited at a normal rate at room temperature. Considering that the diffusion length of the pentacene molecule is important for alignment and that the diffusion length is controlled by the arrival rate of the depositing atoms and by the substrate temperature, one would expect a greater enhancement in the field-effect mobility with a lower deposition rate and a higher substrate temperature. Work to improve the degree of mobility is ongoing. Nonetheless, the ability to control the molecular ordering at a local scale with an IB-treated surface opens up important approaches for the fabrication of high performance OTFTs.

### Conclusions

This article has described the characteristics of pentacene-based TFTs created on anisotropic HfO<sub>2</sub> surfaces using an IB treatment. Both the molecular orientation and the morphology of the pentacene can be controlled, and enhanced mobilities can be successfully achieved. The ultrathin template (20 nm) used as the high-*k* dielec-

tric layer not only promotes self-organization of the pentacene molecules but is also capable of low voltage operation. We believe that further optimization of the IB alignment conditions in OTFT devices will increase the ordering of the pentacene molecules and the mobility. This technique may provide various advantages in circuit design and enhance OTFT performance.

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**Table I.** OTFT characteristics of the field-effect mobilities under the saturation regime for devices with various alignments.

Surface type	Parameters			
	$\mu$ (cm <sup>2</sup> /V s)	$V_T$ (V)	$I$ on/off ratio	SS <sup>a</sup> (V/dec)
Nontreated	$1.1 \times 10^{-3}$	-1.89	$3.32 \times 10^3$	2.9
Perpendicular alignment	$9.6 \times 10^{-4}$	-2.16	$1.83 \times 10^2$	5.2
Parallel alignment	$2.3 \times 10^{-3}$	-1.81	$1.16 \times 10^4$	1.9

<sup>a</sup> Sub-threshold slope.