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Hybrid Organic/ZnO p - n Junctions with n -Type ZnO Grown by Atomic Layer Deposition

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We report on fabrication of hybrid inorganic-on-organic thin film structures with polycrystalline zinc oxide films grown by atomic layer deposition technique. ZnO films were deposited on two kinds of thin organic films, i.e. pentacene and poly(dimethylsiloxane) elastomer with a carbon nanotube content (PDMS:CNT). Surface morphology as well as electrical measurements of the films and devices were analyzed. The current density versus voltage (I - V) characteristics of ITO/pentacene/ZnO/Au structure show a low-voltage switching phenomenon typical of organic memory elements. The I - V studies of ITO/PDMS:CNT/ZnO/Au structure indicate some charging effects in the system under applied voltages.

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1. Introduction

Organic materials are becoming serious competitors of wide band gap semiconductors for some electronics, optoelectronics and solar cell applications. This

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relates to the fact that in some cases, hybrid inorganic/organic material structures are the most prospective devices. For example, coating with transparent wide band gap material can improve time stability of organic LED light emitting devices and can help to reduce costs of solar cells (widely used indium tin oxide is expensive material). For the latter applications strongly *n*-type doped ZnO is required. For most of these applications low thermal budget of growth and post-growth treatment processes is needed, i.e. wide band gap materials appropriate for the above mentioned applications must be grown at low temperature, preferentially at temperature below 200°C to ensure stability of underlying organic films.

The recent works on ZnO films grown by atomic layer deposition (ALD) with reactive organic zinc precursors [1, 2] enabled us to reduce significantly growth temperature of ZnO to temperatures well below 200°C, which in turn allowed us to construct organic/inorganic *p-n* junctions with *p*-type organic material and *n*-type ZnO. Low growth temperature of ZnO allows a configuration of the *p-n* diode with ZnO film at the top of the structure. Two kinds of organic substrates, pentacene and PDMS:CNT, were used for ZnO deposition in the present work. Carbon nanotubes are very promising material for nanoelectronics applications due to their unique electrical properties [3]. Here we analyze topography, electrical and junction properties of the device consisting of *p*-type PDMS:CNT and *n*-type ZnO deposited on the top of the organic film. We also studied pentacene as the organic partner of ZnO in *p-n* junction.

2. Experimental details

A highly conductive indium tin oxide (ITO) film, deposited by rf magnetron sputtering on glass substrates, was used as a bottom ohmic contact for our structures.

Pentacene films were thermally evaporated in a high-vacuum chamber with a pressure of approximately 10^{-6} mbar. Commercially available Aldrich Chemical (98%) pentacene source was used. Before deposition, glass/ITO slides were cleaned precisely in trichloroethylene, acetone, isopropanol and deionized water in sequence by an ultrasonic bath. The films were grown at room temperature and deposition rates of ≈ 5 Å/s.

ZnO films were deposited by atomic layer deposition in two types of reactors, F-120 (Microchemistry) and Savannah 100 (Cambridge NanoTech), using two kinds of zinc precursors: dimethylzinc [$\text{Zn}(\text{CH}_3)_2$, denoted as DMZn] and diethylzinc [$\text{Zn}(\text{C}_2\text{H}_5)_2$, denoted as DEZn], respectively. As an oxygen source we used deionized water vapor. The pressure in the growth chamber was in both reactors at a few millibars.

ZnO films obtained with DMZn precursor were grown at 60°C. Pulsing and purging times for DMZn were both 1.1 s. The pulsing time of water precursor was 0.55 s and the purging time 4.4 s. 2000 pulse/purge cycles were programmed which resulted in 125 nm thick ZnO films.

ZnO layers obtained with DEZn were grown at 100°C. Pulse and purge times for deionized water were 15 ms and 20 s, respectively. For DEZn the analogous times were 60 ms and 8 s. To obtain 80 nm thick ZnO films, 500 pulse/purge cycles were programmed.

ZnO/pentacene structure was obtained with DMZn precursor whereas ZnO/PDMS:CNT structure with DEZn precursor. Prior to ZnO deposition, pentacene as well as PDMS:CNT substrates were annealed at the deposition temperature (60°C and 100°C, respectively) for approximately 30 min.

The surface morphology of ZnO films and organic samples was investigated using atomic force microscopy (AFM) (Veeco, Digital Instruments) in tapping mode.

Au top contacts were deposited on ZnO films by an e-beam evaporator using a shadow mask. The current–voltage characteristics of the ITO/organic film/ZnO/Au junctions were measured by a Keithley 236 Source Measure Unit.

3. Results and discussion

Zinc oxide grows on the substrate as a result of a double exchange reaction $\text{Zn}(\text{C}_2\text{H}_5)_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{C}_2\text{H}_6$

or



for DEZn and DMZn used as Zn precursors, respectively. As we reported recently [2], ZnO films grown at low temperature (60–100°C) show good conductivity ($n \approx 10^{17} \text{ cm}^{-3}$, $\mu_{\text{max}} = 14 \text{ cm}^2/(\text{V s})$), crystallinity and surface smoothness.

Figure 1a shows an AFM image of the pentacene thin film evaporated on ITO/glass substrate. The thickness of the film is 100 nm and the sheet resistance $\approx 10^4 \Omega/\text{square}$. The root mean square (rms) roughness is 16.7 nm and peak-to-valley heights are in the order of the film thickness meaning that the growth dynamics of pentacene layers was rather 3D or multilayer one [4]. The so formed grains have size of approximately 0.4 μm . The annealing of pentacene film prior to ZnO deposition caused a slight increase in pentacene grain size to about 0.6 μm (Fig. 1d). The 125 nm thick ZnO film deposited on pentacene at 60°C formed the grains of size 120–130 nm. We can see in Fig. 1d that the whole pentacene layer was covered by ZnO film. Deposition of ZnO onto thin pentacene film did not cause the increase in surface roughness. Figure 1 demonstrates therefore an important advantage of the ALD technique. Films grown by ALD show very good conformality. They can cover even very developed substrates with uniform film of a defined thickness. This conclusion was supported by our results of electron microscopy investigations performed for P3HT system not discussed here. The similar situation is observed in case of the PDMS:CNT film spin-coated on ITO/glass substrate. In the lower scale (50 \times 50 μm — Fig. 1b) image, we can see that PDMS:CNT forms a wavy-like surface with the wave amplitude of 100–200 nm and the wave period of

about $15\ \mu\text{m}$. But the rms value taken from the $2 \times 2\ \mu\text{m}$ image (Fig. 1c) informs us that the surface is atomically smooth. After deposition of $80\ \text{nm}$ thin ZnO film at 100°C , the surface becomes much more waved, with the wave amplitude $1\text{--}1.5\ \mu\text{m}$ and the period of about $40\ \text{nm}$. This phenomenon can be influenced probably by the relatively high value of the ZnO deposition temperature rather than by the nature of ZnO film, whose thickness is too small to cause such an effect. ZnO, when deposited onto PDMS:CNT substrate, forms the grains $120\text{--}130\ \text{nm}$ wide and about $0.8\ \text{nm}$ high (Fig. 1f), but the surface is still atomically smooth (rms = $0.8\ \text{nm}$). We can conclude that also in the case of elastomer containing carbon nanotubes, ZnO uniformly covered organic material forming organic/ZnO junction.

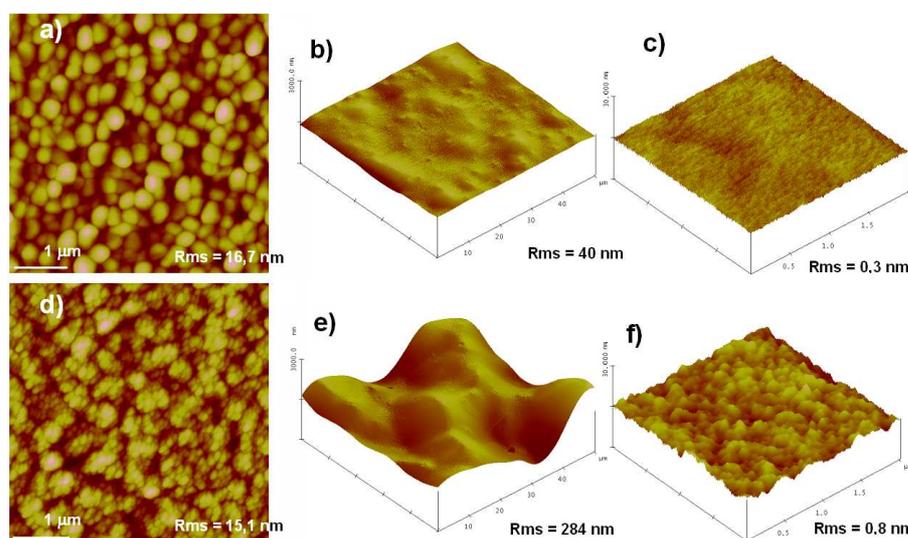


Fig. 1. AFM images of two organic semiconductors: (a) pentacene and (b),(c) PDMS:CNT. (d)–(f) Surface morphology of ALD-deposited ZnO films on these substrates, respectively.

Figure 2a shows current density versus voltage (I – V) characteristics of ITO/pentacene/ZnO/Au structure. A reversible, low voltage switching phenomenon is seen. This is typical of devices which can act as organic memory elements [5]. By sweeping the voltage from $0\ \text{V}$ to $+6\ \text{V}$ and then to $0\ \text{V}$ with respect to the bottom electrode (sweep 1 and 2 in Fig. 2a), a transition to the so-called OFF state, or “erasing” process, takes place. After sweeping the voltage from $0\ \text{V}$ to $-6\ \text{V}$ and then to $0\ \text{V}$ (sweep 3 and 4), the device displays a high conductive state, which can be described as the “writing” process. The ON/OFF current ratio is greater than 30 for voltages ranging between $\pm 1\ \text{V}$. The device current changes polarity at a zero voltage, that indicates the lack of an interfacial space-charge at the diode interfaces [5, 6].

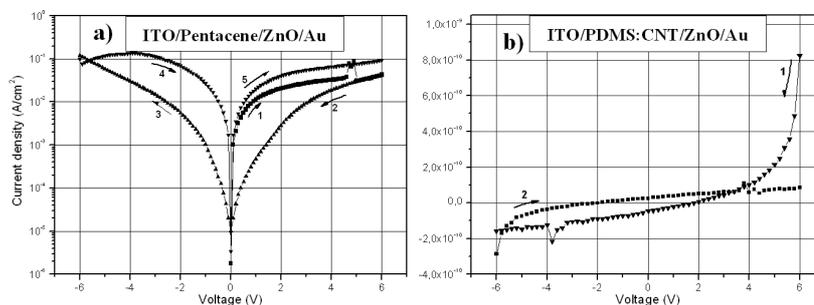


Fig. 2. Current density versus voltage (I - V) characteristics of organic/ZnO hetero-junction devices, ITO/pentacene/ZnO/Au (a) and ITO/PDMS:CNT/ZnO/Au (b).

Some charging effects are observed for ITO/PDMS:CNT/ZnO/Au system (Fig. 2b). Also in this case we can observe, that I - V characteristics show two different dependences related to the applied voltage sweep directions. But, in contrast to ITO/pentacene/ZnO/Au diode, the current changes polarity at a nonzero voltage (+1.8 V for sweep 1 and -1.8 V for sweep 2). One of possible explanations of this phenomenon relates to the ferroelectric properties of ZnO films. In ferroelectric phase a strong dipole moment can appear which causes an internal structure charging. Another explanation is connected with the properties of the PDMS:CNT film. Under applied voltages, a charging of particular carbon nanotubes may occur giving rise to such a characteristics.

4. Conclusions

Low growth temperature available in ALD due to use of DMZn and DEZn as zinc precursors and high conformality of films grown by ALD enabled us the construction of organic/ZnO hybrid structures. Deposition of ZnO onto organic substrates did not cause the increase in surface roughness. This fact, in connection with relatively good electrical parameters of so-deposited ZnO films, makes possible p - n junction formation with good rectifying characteristics. The I - V measurements of ITO/pentacene/ZnO/Au structure show a low-voltage switching phenomenon typical of organic memory elements. The I - V characteristics of ITO/PDMS:CNT/ZnO/Au structure indicates charging effects in the system that may be due to the properties of both ZnO and CNT materials.

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