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Effect of oxygen plasma on the surface states of ZnO films used to produce thin-film transistors on soft plastic sheets

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Electronic displays and flexible electronics are poised to significantly impact emerging industries, including displays, energy products, sensors and medical devices, building a market that will significantly grow in the future. The implementation of transparent electronic devices requires the use of material components that could be formed using controlled deposition in the appropriate orientation onto a transparent flexible substrate. Here, we report a simple and efficient means of depositing onto a flexible polyimide (PI) substrate a highly ordered and highly aligned zinc oxide (ZnO) film for use as a carrier transporting and semiconducting layer with controlled surface charge density for thin-film transistor (TFT) applications. The deposition approach is based on the solution-coating of a zinc-acetate suspension under controlled conditions of the spread flow rate, droplet size of the drops, speed limit, and the oxygen (*ca.* O_2) plasma treatment of the coated film surface on the PI substrate. The plasma surface interactions on the surface states of the ZnO films for various times (*ca.* 1–5 min) were studied using X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Moreover, the effects of O_2 plasma and the subsequent thermal annealing in an O_2 atmosphere at 250 °C on the properties of ZnO films were studied for its efficacy in TFT applications in terms of the charge carrier density and the change in the mobility. ZnO thin-film-based TFTs on PI exhibited a very high electron mobility of 22.8 $cm^2\ V^{-1}\ s^{-1}$ at a drain bias of 5 V after treatment with O_2 plasma for 2 min. Furthermore, the plasma treatment for long durations of time caused a reduction in the charge carrier density from $1.58 \times 10^{19}\ cm^{-3}$ for the 2 min treatment to $1.13 \times 10^{17}\ cm^{-3}$ for the 5 min treatment, and the corresponding electron mobility was changed from 22.8 and 3.1 $cm^2\ V^{-1}\ s^{-1}$ for the treatment times of 2 min and 5 min, respectively. The spin-coating technique used to deposit very thin ZnO films is currently used in microelectronics technology, which helps to ensure that the described ZnO thin-film deposition approach can be implemented in production lines with minimal changes in the fabrication design and in the auxiliary tools used in flexible electronics production.

1. Introduction

Zinc oxide (ZnO) shows great promise as an active layer in thin film transistors (TFTs) due to its exceptional electronic and optoelectronic properties.[1] ZnO is a wide band gap (3.4 eV) II–VI compound semiconductor, which has a stable wurtzite structure with lattice parameters of $a = 0.325$ nm and $c = 0.521$ nm.[2] ZnO is a promising material for short-wavelength light emitting diodes and surface-acoustic wave devices. The high mobility and transparency of ZnO combined with a low temperature deposition process make ZnO a potential candidate for use in flexible and transparent display applications. Notable efforts have been made in recent years to utilize the unique properties of ZnO in a wide variety of applications, including transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics.[3] High-quality ZnO films can be grown at relatively low temperatures (<700 °C). The large exciton binding energy of approximately 60 meV enables an intense near-band-edge excitonic emission at room temperature and above because the exciton binding energy is 2.4 times that of the room temperature thermal energy ($k_BT = 25$ meV).[4] Being inexpensive and nontoxic, ZnO is a good substrate material for devices based on gallium nitride (GaN) due to the good match of the lattice constants.[5] Moreover, ZnO has

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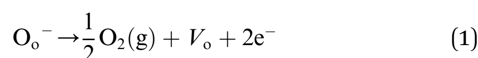
attracted intensive research efforts that are currently directed toward enhanced intrinsic transparent electric conductivity for potential use in the flexible electronics industry. Many of the recent reports featured the integration of ZnO into TFTs on silicon substrates, flexible plastic substrates, and even on stretchable rubber substrates.[6] To achieve many applications in flexible and transparent electronics devices, the development of optimized semiconductor devices using ZnO as a channel layer remains critically dependent on low-temperature processing. ZnO films have been grown using vacuum-based deposition techniques, such as radio-frequency magnetron sputtering,[7] pulsed laser deposition,[8] chemical vapor deposition,[9] atomic layer deposition,[10] transfer printing[11] and sol–gel spin coating.[12] On the basis of these methods, the preparation of ZnO films and a wide variety of oxide semiconductors exhibiting high carrier mobility and low carrier concentrations has been demonstrated for applications in electronic devices.

However, these vacuum-based deposition methods are not likely to be compatible with flexible TFT manufacturing processes due to the need for expensive equipment, the high energy consumption and the low throughput of vacuum-based deposition techniques. High-vacuum and high-temperature based deposition processes are also not well suited for plastic substrates due to their intrinsically low melting temperatures. Moreover, a low manufacturing cost is the primary requirement for modern and mass produced large area electronic devices. Solution-processed thin-film deposition can provide many advantages that facilitate the fabrication of high-performance and low-cost electronics, such as simplicity, low cost, and high throughput. Although the fabrication of a ZnO transistor on a plastic substrate at low temperature has been achieved, significant challenges remain in the fabrication of electronics devices that meet the mechanical and optical specifications for flexible and transparent electronics. For the reasons stated above, we turned our attention to developing a solution-based deposition method to fabricate ZnO thin films. High-quality oxide films can be achieved by solution deposition followed by an O_2 plasma treatment step.[13] Thus, solution deposition followed by a low power (*i.e.*, 20–30 W) O_2 plasma treatment could be a desirable, relatively low-temperature technique for producing high-quality, high-performance ZnO thin films for use in TFT device applications on plastic substrates. In addition to oxygen vacancies, doping can also change the electrical conductivity of ZnO films. Oxygen vacancies, which provide the necessary free carriers for electrical conduction, are easily generated in oxide films.[14] Thus, low power O_2 plasma treatment is expected to be a useful technique to influence the electrical properties of a ZnO-based TFT device fabricated at a relatively low temperature. The carrier concentration could be controlled with the least amount of effort by using O_2 plasma power supply, with the time to create the oxygen vacancies being determined by the following equation:[15]



$$\mathrm{O_o}^- \rightarrow \frac{1}{2}\mathrm{O_2(g)} + V_\mathrm{o} + 2\mathrm{e}^- \quad (1)$$

where e^- denotes an electron, V_o denotes the threshold voltage shift, and O_2 and O_o^- represent the neutral and charged oxygen molecules, respectively, in the ZnO film associated with the TFT device. Moreover, the electrical resistivity (ρ) of ZnO films is determined by the carrier concentration (n) and the carrier mobility (μ) by $\rho = 1/(ne\mu)$, where e is the electron charge.[16] Because 'e' is a constant, to obtain low resistivity, the carrier concentration and carrier mobility should be simultaneously maximized; the methods for achieving the maximum carrier concentration are through the creation of oxygen vacancies and through doping. Oxygen vacancies can be created by controlling the substrate temperature or the ambient oxygen pressure. Note that if an oxygen vacancy is created in a perfect crystal, two electrons are created in the crystal through the contribution from ionized donors. However, if excess oxygen vacancies are created in ZnO thin films, sub-oxides will form, causing the resistivity to increase. The current research studies are mainly focused on achieving low resistivity in ZnO thin films by increasing the free-carrier concentration through use of dopants and oxygen vacancies. Johnson and Horovitz[17] stated that increasing the carrier density *via* doping or oxygen vacancies is self-limiting because increasing the number of free carriers decreases the mobility of the carriers due to carrier–carrier scattering. As a result, our focus is also on the influence of O_2 plasma treatment on the carrier concentrations and on the change in the carrier mobility of ZnO TFTs fabricated on plastic substrates.

In the present study, the influence of O_2 plasma treatment on ZnO films prepared from a solution using a precursor of zinc acetate is studied, as well as its effect on a channel layer in flexible TFTs produced using the treated ZnO films. The various solution-deposition and O_2 plasma treatment conditions were carefully controlled and systematically studied, from the preparation of the precursor solution to the plasma surface interaction, to investigate the effects of each of the conditions. This study is focused on increasing the free-carrier concentration in thin films through the use of dopants and oxygen vacancies created by plasma surface treatment. The interaction of the plasma ions with the surface of the films on the molecular level was investigated using FTIR spectroscopy to determine the chemical composition and using XPS spectra for the O1s and C1s regions to determine the surface states. The O_2 plasma exhibited a strong effect on the charge carrier density and caused a change in the mobility of the ZnO TFTs. Because the O_2 plasma treatment primarily affects the surface of the films, the effect of this treatment is expected to be enhanced in systems with a high surface-to-volume ratio. The O_2 plasma treatment plausibly reduced the surface dangling bonds and the carbon contaminations, thereby forming the oxygen vacancy-rich surface. The characteristics of the ZnO TFTs, including the threshold voltage shift and the carrier mobility, were changed by the O_2 plasma treatment. The purpose of this work is to demonstrate the possibility of producing a high-mobility flexible and transparent TFT with improved performance through a sol–gel process that is highly compatible with the other standard fabrication techniques.

2. Experimental section

2.1 Preparation of ZnO thin-films

The precursor solution for producing the ZnO thin film to be used as a channel layer was prepared by dissolving zinc acetate

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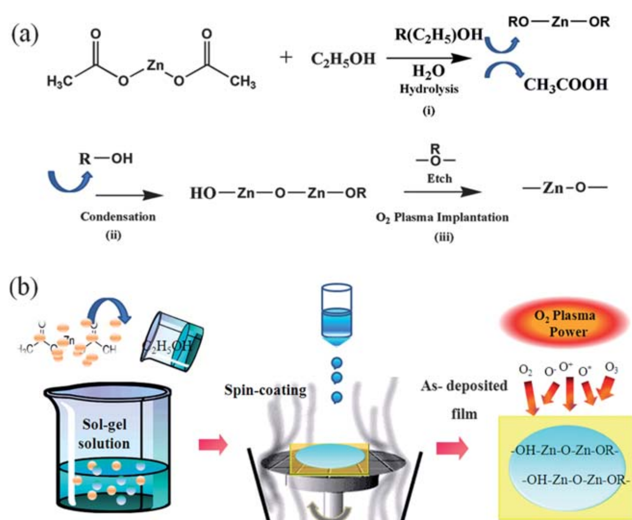
dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$, Aldrich, St. Louis, MO] into ethanol, abbreviated as EtOH [CH_3CH_2OH; Fluka; water content <0.1%; Aldrich]. The concentration of zinc acetate was 0.05 M, and the volume of EtOH was 10 mL. The solution was rigorously stirred for 1 h at 60 °C and filtered through a 0.22 μm membrane filter [polytetrafluoroethylene (PTFE)] to obtain a transparent and homogeneous solution. Prior to thin film deposition, a DuPont Kapton® PI film of 38 μm thickness was chosen from the PV9100 series for use as the flexible substrate to fabricate the ZnO TFT and for the ZnO used for other characterizations. The PI substrate was ultrasonically cleaned using EtOH for 15 min and then rinsed with DI water for 10 min. Next, a high-pressure stream of N_2 gas was used to remove the water and any remaining particles from the PI surface. The cleaned PI substrate was then annealed at 200 °C for 1 h under vacuum to achieve relative thermal stability and to enhance the adhesion strength. The precursor solution of zinc acetate was spin coated at a speed of 500 rpm for 30 s and at 1000 rpm for 20 s onto the flexible PI substrate, with a piece of glass substrate being used to support the PI. The O_2 plasma treatment was applied immediately after the spin coating to obtain a pure ZnO thin film and to remove any unnecessary organic impurities. The as-deposited films were treated with O_2 plasma for 1 to 5 min in an O_2 plasma reactor (Harrick Scientific Corp., Japan), which supplied a plasma power of 18 W. Scheme 1(a) illustrates the expected three-step reaction of (i) hydrolysis, (ii) condensation, and (iii) O_2 plasma surface ion interaction for producing an appropriate ZnO film on a flexible PI substrate. Scheme 1(b) shows a rough schematic of the preparation of the zinc acetate sol–gel solution, the spin coating process and the surface O_2 plasma treatment. This scheme includes the successive removal of the hydroxide layer and organic impurities with the O_2 plasma treatment. These O_2 plasma-treated films were also annealed at a temperature of 250 °C for 1 h under normal environmental conditions for surface passivation.



Scheme 1 (a) Schematic representation of the reaction of zinc acetate mixed into ethanol and the O_2 plasma growth mechanism for the fabrication of ZnO thin-films; (b) process of making the sol–gel solution, spin-coating the solution to fabricate the thin film, and finally using O_2 plasma processing to modify the conductivity.

2.2 ZnO thin-film characterizations and TFT device fabrication

The surface morphology of the ZnO films on flexible PI substrates was evaluated using atomic force microscopy (AFM) with a Digital Instruments Nanoscope D-5000 at a scan size of 2 μm and a scan rate of 1 Hz. The surface roughness characteristics of these O_2 plasma treated films were calculated in terms of the average root-mean square (rms) using AFM data processing software. The thicknesses of the ZnO films on the PI substrate were measured using a step-profilometry technique. The optical absorption of the ZnO films on flexible PI substrates was measured at wavelengths between 300 nm and 900 nm using a UV-Vis absorption spectrometer. X-ray photo-spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR, Bomem DA-8.3) analyses were also used to confirm the effects of the plasma treatment time (from 1 min to 5 min) on the surface properties of the ZnO films and its interaction with the surface ions. To fabricate the ZnO TFTs on flexible PI substrates, these O_2 plasma-treated films were used as the active layer for the channel on a SiO_2/Au/Cr/PI substrate. To fabricate the transistor with bottom-contact electrodes, Cr and Au with thicknesses of 20 and 80 nm, respectively, were sequentially deposited through a shadow mask using a thermal coater to function as the gate electrodes. Then, the 100 nm thick SiO_2 film was deposited using the plasma-enhanced chemical vapor deposition (PECVD) technique as a gate insulator layer. Finally, the source and drain electrodes of Au with a thickness of 100 nm were deposited onto the ZnO/SiO_2/Au/Cr/PI through a shadow mask, which yielded the top-contact for the ZnO TFTs. The channel length (L) and width (W) were 70 μm and 2000 μm, respectively. The electrical measurements for the ZnO TFT devices were performed using an Agilent-4156 probe station.

3. Results and discussion

3.1 ZnO film analysis: surface roughness, thickness and transmittance properties

The AFM images, displayed in Fig. 1(a)–(e), show that the O_2 plasma-treated ZnO films are well dispersed and micro-crystalline, when deposited on flexible PI substrates. The AFM images of the surface treated with O_2 plasma power for 1–5 min are essentially smooth and uniform surfaces. The average rms surface roughness values of the ZnO thin-films treated with O_2 plasma for 1–5 min were 1.12 nm (1 min), 1.28 nm (2 min), 1.53 nm (3 min), 1.92 nm (4 min) and 2.17 nm (5 min). This result indicated that the ZnO films treated with O_2 plasma for 1–5 min exhibited good large-area quality, smoothness, a crack-free morphology and a uniform surface. The variation in the surface properties of the samples treated with O_2 plasma for 1–5 min is clearly observed in the AFM images. For 1–3 min of plasma treatment, the film surface exhibited a dense and deep microcrystalline nature. However, as the plasma treatment time increased to 4 to 5 min or more, the quality of the film surface

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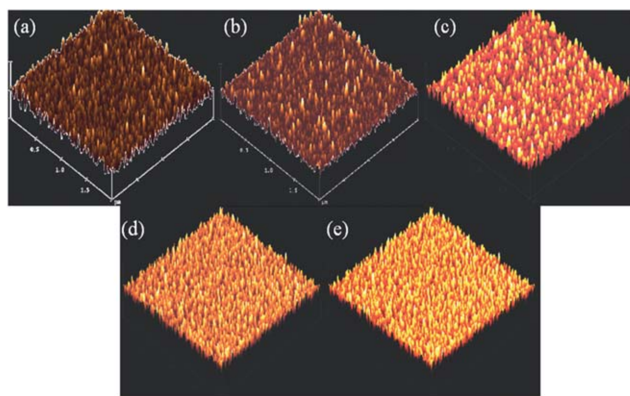

Fig. 1 (a–e) AFM images (scale: 2 μm × 2 μm) of the ZnO films for the samples after O_2 plasma treatments ranging from 1 to 5 min in duration.

degraded. The extended plasma treatment etched the native surface particles, including the organic residuals. The extended plasma treatment is also expected to degrade the charge carrier concentration and the mobility of the transistor device. Moreover, the surface morphology of our plasma-treated films deposited onto flexible PI substrates exhibits similar effects to those of O_2 plasma pre-treatment on ZnO thin films grown on a polyethersulfone substrate at various deposition temperatures.[18] The AFM results demonstrated the unique ability of these films with a microcrystalline surface to be used in device applications on a flexible substrate to control the functionality of ZnO TFTs. Moreover, the O_2 plasma treatment plausibly reduces the surface dangling bonds and the carbon contamination, thereby resulting in an oxygen vacancy-rich surface. The roughness and –O–Zn– bonds to the –O–OH– could be slightly increased, but the post-annealing ambient has no further significant effect on the morphology, except for the passivation of the surface. After the O_2 plasma treatment, the relative density of the –O–Zn– bonds was enhanced and that of the –O–OH– bonds decreased as the treatment time increased. Furthermore, for the use of O_2 plasma for a treatment time of 5 min or more, the surface residuals and the –O–Zn– bonds were seriously affected, which is expected to degrade the device properties.

The thicknesses of the ZnO films on flexible PI substrates were measured using a step-profilometry method: 12.1 nm for 1 min O_2 plasma, 11.6 nm for 2 min O_2 plasma, 11.2 nm for 3 min O_2 plasma, 10.4 nm for 4 min O_2 plasma and 10.2 nm for 5 min O_2 plasma. A minor reduction in the thickness of the ZnO films with increasing plasma treatment time was observed. Apparently, as the plasma strikes the surface of the ZnO films, it engraves the surface particles. This engraving could be due to etching of organic residuals, which results in the reduction of the film thicknesses. To confirm the transmittances of ZnO thin films on flexible PI substrates as well as on glass substrates as a function of O_2 plasma treatment time, we deposited an ultrathin ZnO film onto a flexible PI substrate that covers the university NCTU logo. The average optical transmission of the PI substrate in the visible part of the spectrum is approximately 88%, as shown in Fig. 2, which indicates a 12% transmission

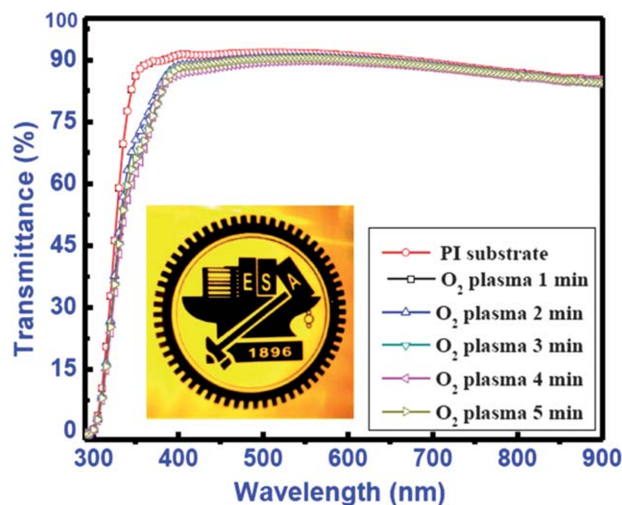

Fig. 2 Transmission spectra for transparent ZnO thin films on PI; inset: the ZnO film over the university NCTU logo.

loss from the ZnO-coated flexible PI substrate. High optical transmittance over a large wavelength range from 350 nm to 750 nm is an important property for the transparent or semitransparent ZnO layer in TFTs because one must minimize any optical loss due to the transparent semiconductor layer. The ZnO film on a PI substrate exhibits a slightly lower transmittance compared with the ZnO film on glass for different O_2 plasma process treatments, but this lower transmission is compensated for by its slightly lower sheet resistance (27.2 $\Omega\ sq^{-1}$), indicating that the transmittance to sheet resistance ratio is similar for ZnO on either substrate. In addition to the high optical transparency on par with ZnO thin films over flexible substrates, solution-deposited ZnO offers excellent mechanical flexibility while maintaining high conductivity, a significant advantage over a traditional semiconductor layer that will crack under a large degree of bending. The mechanical flexibility and recoverable conductivity of this ZnO semiconductor layer not only makes it compatible with low-cost, roll-to-roll manufacturing but also helps it find promising applications in emerging technologies (such as foldable displays, flexible solar cells, and TFTs), in which the semiconductor layer must withstand mechanical deformation without a loss in conductivity. Transparent ZnO thin films on glass and on flexible substrates have been widely studied, and our experimental results have determined the transmittance functions of a ZnO thin film.[19]

3.2 Effect of O_2 plasma treatment on the surface properties of ZnO films: XPS and FTIR analyses

To determine the effect of plasma-induced active oxygen ions on the electrical properties of ZnO TFTs, we used XPS to analyze the surface of the ZnO after plasma treatment. The XPS data indicate that the O1s peak at the ZnO surface can be consistently fitted by three Gaussians, centered at 532.4 (O_I), 531.2 (O_{II}) and 530.4 eV (O_{III}). Fig. 3 shows that the relative intensity of oxygen continuously increases towards higher binding energies as the plasma-treatment time increased from 0 to 3 min, indicating a

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clear increased concentration of the oxygen chemical state on the ZnO surface. However, the relative intensity of O_2 reverses for treatment times longer than 3 min because the active oxygen ions reacted with residual hydrocarbons at the surface of the ZnO film.[20] The XPS data indicate that the peak intensity decreased. The high binding energy component located at 532.4 eV is usually attributed to the presence of loosely bound oxygen on the ZnO surface, such as $-CO_3$, adsorbed H_2O, and adsorbed O_2. The oxygen components were observed to increase after the ZnO film was treated with O_2 plasma for 1 min. The results implied that the O_2 plasma caused an accumulation of absorbed O_2 on the ZnO surface with increasing treatment time. The medium binding energy component, which is centered at 531.2 eV, is associated with oxygen deficient regions within the matrix of ZnO.[21] The intensity changes of the medium oxygen component are related to variations in the concentration of oxygen vacancies. In other words, medium oxygen-related oxygen vacancies provide free electrons in the active channel layers of ZnO TFTs. The intensity of the medium oxygen related to oxygen vacancies was reduced by the O_2 plasma treatment of 3 min. The low binding energy component (*i.e.*, third energy component) of the O1s spectrum at 530.4 eV is attributed to O^{2-} ions within the micro-crystalline structure of the hexagonal Zn^{2+} ion array. In other words, the intensity of the third energy component is a measure of the amount of oxygen atoms in a fully oxidized stoichiometric surrounding. Thus, we concluded that an O_2 plasma treatment of 5 min or more resulted in the reaction of active oxygen ions with the residual hydrocarbon in the ZnO film and in the etching of the Zn^{2+} ion array. This reaction and etching affect the semiconducting properties of the ZnO surface and consequently degrade the ZnO TFT performance to lower the mobility. This degraded performance indicates that the number of –OH–Zn–O–Zn–OR– bonds increased and the O–OH and –Zn–OR– bonds lost from the surface were transformed into Zn–O– bonds, meaning that the ZnO was formed at the Zn surface after the O_2 plasma treatment.

In addition, XPS analysis was performed to identify the chemical reactions on the carbon surface of the zinc acetate precursor-based films on the flexible PI substrate resulting from O_2 plasma treatment. The XPS analysis was conducted for the C1s peaks for the untreated film and films treated using O_2 plasma for durations ranging from 1 to 5 min. The XPS survey spectra of the untreated and plasma-treated carbon fibers exhibited prominent peaks of carbon in the binding energy range of 270–295 eV. Fig. 4 shows the original and the deconvoluted C1s core level spectra of the untreated and plasma-treated carbon fibers. For the untreated sample, the C–C peak was located at 284.7 eV, C–OH at 285.9 eV, C–O–C at 286.1 eV, C=O at 287.5 eV, and the COOR or COOH group at 288.8 eV. The C–O–C and COOR peak area ratios increased, accompanied by a decrease of the C–O peak area after the plasma treatment. When the O_2 plasma was used for durations ranging from 1 to 5 min, shifts in the binding energy were observed, with the peak shifting towards the chemical shift for native carbon peak. The change is clearly observed between the untreated sample and

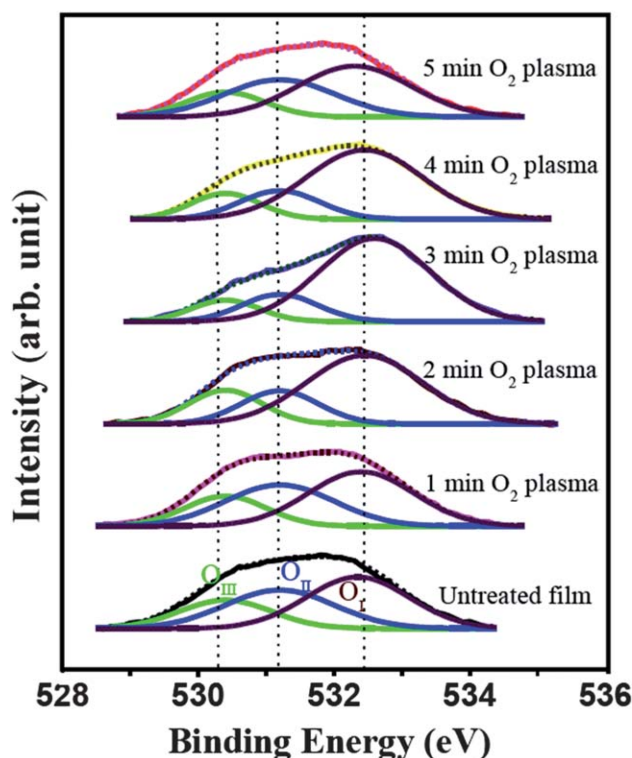

Fig. 3 XPS spectra of the O1s region of ZnO films for O_2 plasma treatments with durations from 0 to 5 min.

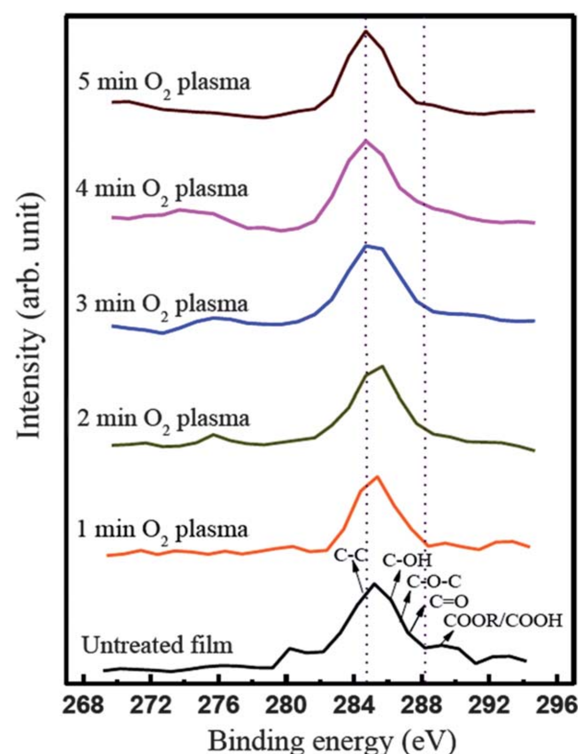

Fig. 4 C1s spectra for untreated and O_2 plasma-treated films on flexible PI substrates.

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the samples that were treated with O_2 plasma for durations ranging from 1 to 5 min. This observation confirmed that the plasma treatment increased the oxidation of the fiber surfaces, transforming C–O groups into C=O and COOR groups. The XPS spectra of the C1s region yielded five major peaks composed of five components, of which the binding energies of C–C and C–H were normally assigned at 284.6–285.8 eV. Chemical shifts in the binding energy are usually assigned for each functional group, such as C–O, C=O, and COOH. Thus, the plasma treatment makes the support surface rich in oxygen functional groups. These three C1s peaks (284.7, 285.9, and 288.8 eV) are attributed to adventitious surface contamination arising from (CH_x)-like carbon and carbon oxides. For the O_2 plasma treatment and the subsequently annealed films (at 250 °C), complicated and unassigned peaks were observed with core level carbon peaks of C–C and C–H at 284.6 eV. These assignments from data on a flexible PI substrate are in agreement with the observed C1s core level peaks.[22] The O_2 plasma treatment leads to the creation of active species and free radicals on the carbon support during the plasma treatment. Weak or unstable boundary layers on the surfaces of the carbon supports are removed by the O_2 plasma treatment. Thus, such changes easily introduce oxygen functional groups onto the surface of the carbon supports. However, using a plasma power for a longer duration results in etching of the –Zn–O– surface, which affects the electrical performance of the film. We have examined these effects on a ZnO film used in a TFT application to demonstrate the tuning of the carrier mobility with facile O_2 plasma. From these analyses and the measured electrical properties from the ZnO-TFT devices, we conclude that only short duration plasma treatments enhance the properties of the ZnO thin film-based electrical devices.

FTIR spectroscopy was used to examine the functional groups in the spectrum of the ZnO precursor film prepared from zinc acetate dissolved in ethanol to gain more insight into the effect of the O_2 plasma treatment. Fig. 5 shows the FTIR absorption spectrum of the as-deposited (*i.e.*, ZnO precursor film) and the O_2 plasma-treated films for treatment durations of 1–5 min on PI substrates. For the untreated sample, the band at 3418 cm^{-1} is due to O–H species and the absorbed water molecules in the film, and the band at 29 100 cm^{-1} is due to C–H stretching frequencies. The band observed at 1592 cm^{-1} is due to C=O arising from the bridging-type bond turning into acetate bonding ($OCOO^-$). The bands at 1430 and 1015 cm^{-1} are due to the C–O stretching frequencies, and the band at 1330 cm^{-1} is due to weakly bound acetate molecules (HOOC–R), which is consistent with the previous reports.[23] The band observed at 450–580 cm^{-1} is due to the Zn–O stretching frequencies.[24] For a sample treated with O_2 plasma for 1 min, the spectra were nearly identical with those of an untreated sample, except that the O–H band shifted slightly towards lower frequencies. The spectra of ZnO precursor films treated with O_2 plasma for 2–5 min exhibited an absence of absorption bands corresponding to organics and hydroxyls, indicating the complete removal of the organics and hydroxyls. According to the XPS spectra shown in Fig. 4, most of the organic part of the CH_3COO group of zinc acetate and other volatile parts (C–H, O–H, C–O, *etc.*) were removed for O_2 plasma treatments with durations from 2 to 5 min. These FTIR spectral results clearly confirmed that the bonding force of the acetate anion with zinc cations decreases with the phase transformation, the OH-groups gradually replaced the acetate groups coordinated to the matrix zinc cations, and the acetate groups were finally released completely, thus enabling ZnO to be formed with the release of the acetate anion.

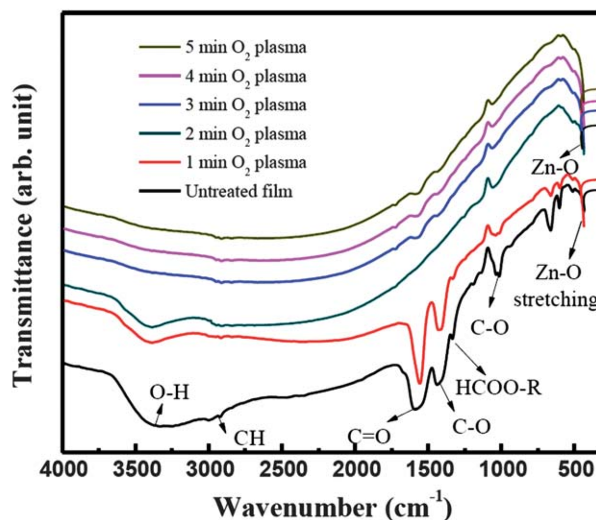

Fig. 5 FTIR spectra for untreated and O_2 plasma-treated films on flexible PI substrates.

3.3 Effect of the O_2 plasma on the electrical properties and the charge carrier density of the ZnO TFTs fabricated on flexible PI substrates

To comprehensively investigate the application and the effects of the O_2 plasma-treatment on ZnO films to be used as the active semiconductor layer in TFTs, we used the TFT device configuration shown in Fig. 6(a), which was also used to determine the O_2 plasma treatment effect on mobility. A high-quality optical image of the TFT devices on a flexible PI substrate is shown in Fig. 6(b). Fig. 6(c) shows the transfer characteristics of the plasma-treated ZnO TFTs of samples that underwent treatment with O_2 plasma for durations ranging from 1 to 5 min. The I_{on}/I_{off} ratio is 10^8 with a mobility of 0.74 $cm^2 V^{-1} s^{-1}$ for the sample treated with O_2 plasma for only 1 min. As the plasma power was used for a longer duration, the off-state leakage currents (I_{off}) of the ZnO TFTs of the plasma-treated samples, which were treated for durations ranging from 1 to 2 min, exhibited significant improvement from 1.86×10^{-11} A to 5.90×10^{-12} A and hence an increase in the I_{on}/I_{off} ratio from 10^7 to 10^9, while the mobility increased to 22.8. However, the degradation of I_{off} indicates considerable changes in the carrier concentration and distribution after O_2 plasma treatment for 2 min. The I_{off} level increased by over two orders of magnitude for plasma treatment durations increasing from 3 to 5 min, which consequently degraded the ZnO-TFT performance by decreasing the mobility. To understand the performance of the ZnO TFTs with various

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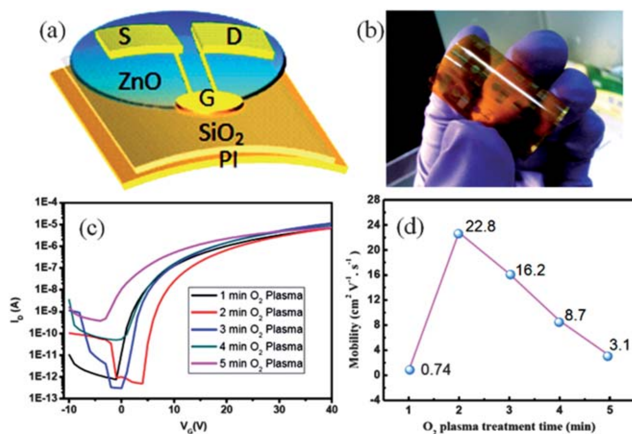

Fig. 6 (a) Schematic configuration of the ZnO-based TFT structure on a PI substrate, (b) an optical image showing the TFTs on a flexible PI substrate, (c) transfer (I_D–V_G) characteristics measured at a constant $V_D = 5$ V for O_2 plasma treated ZnO precursor films for different treatment durations ranging from 0 to 5 min, and (d) a plot of the variation in mobility for different treatment durations ranging from 1 to 5 min.

O_2 plasma treatment durations, the extracted TFT-device parameters are listed in Table 1. The saturation mobility in the thin-film transistors was generally estimated using the following equation:[25]

$$I_D = \frac{W}{2L}\mu_{sat}C_i(V_G - V_{th})^2 \quad (2)$$

where μ_{sat} is the field-effect charge carrier mobility, C_i is the capacitance per unit area of the dielectric, V_{th} is the threshold voltage, and W and L are the ZnO TFT's channel width and length, respectively. In Fig. 6(d), a curve is also shown for the variation in mobility at different treatment times, ranging from 1 to 5 min, for the ZnO films used as a channel layer. As described in Table 1, the ZnO TFT sample treated with O_2 plasma for 1 min exhibited a good saturation mobility, threshold voltage and I_{on}/I_{off} ratio. However, the ZnO TFTs treated by O_2 plasma for 2 and 3 min exhibited excellent saturation mobilities, which were 10 times greater than the mobility of the sample treated for 1 min under plasma power. Similar reductions in I_{off}, V_{th} and mobilities were observed for the ZnO TFT devices with the ZnO film surface treated with plasma power for 5 min or longer. This degradation can be interpreted as the adsorption of highly electronegative active O_2 ions that affect the depletion layer in the ZnO film. Remote O_2 plasma treatments at 18 W for 5 min or longer led to a shift in the turn-on voltage and a reduction in the off-current by more than two orders of magnitude in the ZnO thin film transistors. The effect of O_2 plasma power on solution-processed ZnO film used into TFTs application by XPS analyses is supported by results from the changes in the mobilities with time duration of the O_2 plasma process.

Moreover, the effect of the O_2 plasma can also be interpreted as the adsorption of active oxygen ions with highly electronegative effects on the depletion layer in the ZnO film. The carrier mobilities of the ZnO TFTs can be used to calculate the charge carrier concentrations using the equation[26]

$$n = \frac{I_D L}{q V_D \mu_{sat} W d} \quad (3)$$

where n is the carrier concentration, I_D is the measured drain current at V_D, L is the channel length, W is the channel width, d is the gate insulator thickness, q is the electron charge, and μ_{sat} is the carrier mobility. The carrier concentrations for the ZnO thin-films treated with O_2 plasma treatments for durations of 1–5 min were calculated as 1.52×10^{17} cm^{-3} for the 1 min sample, 1.58×10^{19} cm^{-3} for the 2 min sample, 4.3×10^{18} cm^{-3} for the 3 min sample, 1.75×10^{18} cm^{-3} for the 4 min sample and 1.58×10^{17} cm^{-1} for the 5 min sample. The resulting charge carrier concentration first increased for the samples with 1 to 2 min treatments and then decreased for the samples with 3 to 5 min treatments. Further O_2 plasma treatment of longer than 5 min resulted in devices with carrier concentrations that decreased as the O_2 ratio increased. This observation could be due to the oxygen vacancies compensated by oxygen, causing the channel layer to be less conductive by reducing the supply of free electron carriers to the conduction band. In other words, a higher O_2 ratio induces a lower density of oxygen vacancies, which usually act as shallow donors. The remaining electrons of the deposited ZnO film should be lower for a film with a high O_2 ratio caused by O_2 plasma treatment of longer duration (3–5 min) than for a film with a low O_2 ratio (*i.e.*, low O_2 plasma treatment time).[27] Moreover, the interaction among the O_2 plasma surface ions and the oxygen vacancies influences the carrier concentration in a positive manner.

Fig. 7(a)–(e) show the output characteristics for ZnO film-based transistors treated using the O_2 plasma process for 1–5 min. A good ohmic contact property at the ZnO interfaces is observed for all samples due to the nearly identical switching on drain current (I_D) at 1 V drain voltage (V_D). Under various gate voltages, all the drain currents sharply increase with a drain voltage in the range of 1–5 V, gradually increase with a drain

Table 1 Various electrical parameters of ZnO TFTs on flexible PI substrates treated with different O_2 plasma surface treatment durations ranging from 1 to 5 min

O_2 Plasma-treatment time (min)	I_{on} (A)	I_{off} (A)	I_{on}/I_{off} ratio	V_{th} (V)	μ_{sat} (cm^2 V^{-1} s^{-1})
1	2.46×10^{-4}	1.86×10^{-11}	10^7	13.9	0.74
2	8.26×10^{-3}	5.90×10^{-12}	10^9	12.9	22.8
3	6.48×10^{-3}	6.39×10^{-12}	10^9	11.5	16.2
4	3.11×10^{-3}	3.96×10^{-11}	10^8	13.2	8.7
5	1.25×10^{-3}	6.84×10^{-10}	10^6	10.9	3.1

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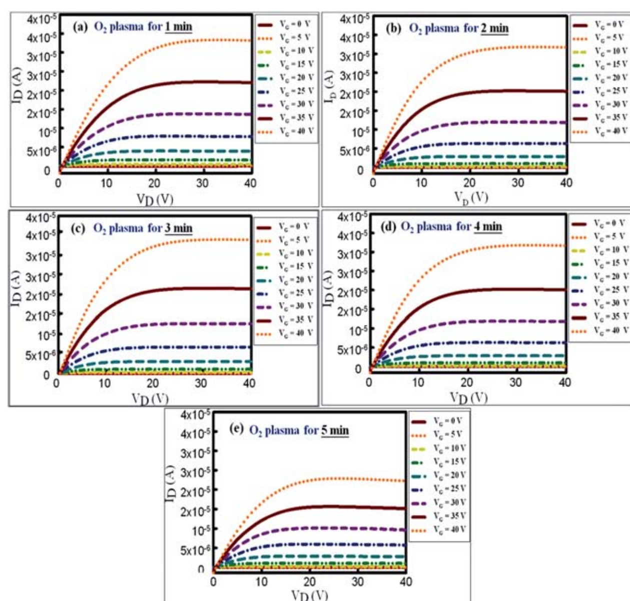

Fig. 7 (a–e) Output characteristics (I_D–V_D) for O_2 plasma-treated ZnO channel layers prepared at different treatment times ranging from 1 to 5 min; the gate bias (positive voltage) ranges from 0 to 40 V.

voltage in the range of 5–20 V, and saturate with a drain voltage in the range of 20–40 V. Upon repeated sweep tests, the ZnO TFTs exhibit consistent performance, with a clear linear curve and saturation behaviors. This observation reflects the lack of degradation of the device performance from repeated I_D–V_D tests only for the 1–2 min O_2 plasma process. Furthermore, upon increasing the duration of the plasma power to 3 to 5 min or longer, the maximal output drain current at a gate voltage of 28 V is first increased for treatment durations ranging from 1 to 3 min and then decreased from 3 to 5 min. The low saturation currents and carrier mobilities of ZnO TFTs with the ZnO film treated by O_2 plasma for longer durations of approximately 5 min or longer are caused by the large barrier heights for electron injection at the Au/ZnO interface after O_2 plasma treatment. This phenomenon was explained in the previous section as most likely being due to the number of electrons, oxygen vacancies and carrier scattering effect. Therefore, the annealing temperature strongly affects the output performance of the ZnO TFTs, and the selection of a suitable annealing temperature is a very critical parameter for zinc acetate solution-processed ultrathin film transistors in future industrial applications. We conclude that the electrical properties from our solution-deposited ZnO TFTs over flexible substrates are best for ZnO films treated by the low power plasma process for durations of up to 3 min; this result is similar to the previously published results of ZnO TFT's properties over other substrates.[28]

3.4 Model for O_2 plasma treatment of the ZnO film surface and the energy band diagram

Because of the uncertain knowledge of the conductive processes in eosin and ZnO films, the incorporation of the experimental results into a model for sensitization must be speculative. O_2 plasma is known to contain various oxygen ions and radicals, such as O^+, O^-, O^{2+} and O*, especially with the atomic radical as the main species.[29] The oxygen radical atoms, O*, are then expected to fill oxygen vacancies during diffusion through the ZnO bulk, reducing the free carrier concentration and thus the dark current level. Based on these observations, we designed a possible model of O_2 plasma for the threshold voltage shift depending on the oxygen ratio, as shown in Fig. 8(a), and further studied how this effect is explained by an energy band diagram model, as illustrated in Fig. 8(b).

The properties of the ZnO TFTs were highly influenced by oxygen ions during their O_2 plasma surface interaction, which may be because of oxygen vacancies that provide the needed free carriers for electrical conduction because oxygen vacancies could be easily generated in the oxides.[30] Fig. 8(a) shows the schematic mechanisms for the proposed O_2 desorption model under O_2 plasma for a ZnO thin film. The O_2 concentration effect on a ZnO thin film is described for the control of the threshold voltage (V_{th}) parameter due to varying O_2 treatment. This description involves understanding how the oxygen ratios influence the electronic properties and how the electronic behavior can be controlled. The O_2 adsorbed on the ZnO film, which can capture electrons in the back channel, exists as O^{2-} in the form of $O_2 + e^- \rightarrow O^{2-}$, leading to a decrease in the carrier concentration of the ZnO film and an increase in the V_{th} shift. The properties of the ZnO TFTs were highly influenced by the O_2 plasma surface interaction, which may be because of the oxygen vacancies provide the necessary free carriers for electrical conduction in ZnO film used as the conducting medium. However, under O_2 plasma treatment for longer durations (>5 min), the electrons generated from the plasma induce electron–hole pairs that react with the absorbed O_2, thus reducing O_2 in the back channel and resulting in a V_{th} shift because the energy barrier is proportional to the square of the density of surface trap states at the grain boundaries and inversely proportional to the free charge carrier density. The observed decrease in charge carrier mobility is associated with either a decrease in the charge carrier density or an increase in the surface trap density.[31] Thus, we conclude that a reduction of charge carrier density occurs due to the oxygen adsorbed on ZnO surfaces. Furthermore, the adsorption of oxygen at the grain boundaries could also lead to an increase in the surface trap state density at the grain boundaries, which would also increase the barrier

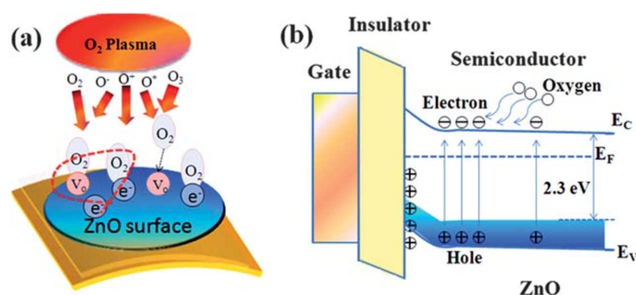

Fig. 8 (a) Possible model of the effect of O_2 plasma for the threshold voltage shift dependence on the oxygen ratio. (b) Energy band diagram illustrating the photo-electric process details in an *n*-channel ZnO-TFT including the behavior of interface trap charges under O_2 plasma.

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height and thus reduce the charge carrier mobility. Fig. 8(b) shows the energy band of the ZnO TFTs under O_2 plasma treatment. The subgap electron excitation can occur from the deep-subgap to the conduction band under oxygen ions when the O_2 plasma provides sufficient energy (>1.7 eV), resulting in increases in the free electron concentration in the ZnO film. However, the electron concentration is seriously affected for O_2 plasma treatments of longer duration. All the characterized ZnO TFTs with the long duration O_2 plasma treatment exhibit a reduced free charge carrier density and thus a lower carrier mobility.

4. Conclusion

The recent advances in transparent flexible TFTs have highlighted the use of low-cost technology and materials to replace the most commonly used semiconductor materials. We have successfully used a simple and cost-effective technique for preparing ZnO films, which includes a spin-coating technique using a zinc-acetate precursor solution and a low power O_2 plasma process. A high-mobility ZnO TFT on a flexible PI substrate was demonstrated with an O_2 plasma process duration of 2 min. Moreover, the ZnO precursor film treated with O_2 plasma for 1–5 min confirmed the significant changes in the electrical properties of the ZnO TFT caused by the active oxygen ions reacting with residual hydrocarbons and the production of excess oxygen vacancies near the Zn atoms. We demonstrated the unique ability of adjusting the charge carrier concentration of ZnO of the microcrystalline layers by controlling the humidity in which the thermal annealing at 250 °C step was performed after the O_2 plasma treatment. With all these benefits shown above, we believe that the present work demonstrates an efficient pathway for realizing the full potential of transparent flexible TFTs in the near future.

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Notes and references

1 A. Janotti and C. G. van De Walle, *Rep. Prog. Phys.*, 2009, **72**, 126501.

2 (*a*) Z. L. Wang, X. Y. Kong, Y. Ding, P. Gao, W. L. Hughes, R. Yang and Y. Zhang, *Adv. Funct. Mater.*, 2004, **14**, 943; (*b*) N. K. Hassan, M. R. Hashim, Y. Al-Douri and K. Al-Heuseen, *Int. J. Electrochem. Sci.*, 2012, **7**, 4625.

3 (*a*) Y.-S. Choi, J.-W. Kang, D.-K. Hwang and S.-J. Park, *IEEE Trans. Electron Devices*, 2010, **57**, 26; (*b*) K. Laurent, B. Q. Wang, D. P. Yu and Y. Leprince-Wang, *Thin Solid Films*, 2008, **517**, 617; (*c*) O. Maksimov, *Rev. Adv. Mater. Sci.*, 2010, **24**, 26; (*d*) M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, *Science*, 2001, **292**, 1897; (*e*) B. K. Roberts, A. B. Pakhomov, V. S. Shutthanandan and K. M. Krishnan, *J. Appl. Phys.*, 2005, **97**, 10D310.

4 Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho and H. Morkoç, *J. Appl. Phys.*, 2005, **98**, 041301.

5 P. K. Shishodia, H. J. Kim, A. Wakahara, A. Yoshida, G. Shishodia and R. M. Mehra, *J. Non-Cryst. Solids*, 2006, **352**, 2343.

6 (*a*) K.-S. Jang, D. Wee, Y. H. Kim, J. Kim, T. Ahn, J.-W. Ka and M. H. Yi, *Langmuir*, 2013, **29**, 7143; (*b*) S. Y. Cho, Y. H. Kang, J.-Y. Jang, S. Y. Nam, J. Lim, S. C. Yoon, D. H. Choi and C. Lee, *Chem. Mater.*, 2012, **24**, 3517; (*c*) Y. Jung, T. Jun, A. Kim, K. Song, T. H. Yeo and J. Moon, *J. Mater. Chem.*, 2011, **21**, 11879; (*d*) K. Kim, S. Park, J.-B. Seon, K.-H. Lim, K. Char, K. Shin and Y. S. Kim, *Adv. Funct. Mater.*, 2011, **21**, 3546; (*e*) S. Y. Park, B. J. Kim, K. Kim, M. S. Kang, K.-H. Lim, T. I. Lee, J. M. Myoung, H. K. Baik, J. H. Cho and Y. S. Kim, *Adv. Mater.*, 2012, **24**, 834.

7 (*a*) E. M. C. Fortunato, P. M. C. Barquinha, A. C. M. B. G. Pimentel, A. M. F. Gonçalves, A. J. S. Marques, L. M. N. Pereira and R. F. P. Martins, *Adv. Mater.*, 2005, **17**, 590; (*b*) C. C. Liu, M. L. Wu, K. C. Liu, S.-H. Hsiao, Y. S. Chen, G.-R. Lin and J. J. Huang, *IEEE J. Display Technol.*, 2009, **5**, 192.

8 J. B. Franklin, B. Zou, P. Petrov, D. W. McComb, M. P. Ryan and M. A. McLachlan, *J. Mater. Chem.*, 2011, **21**, 8178.

9 D. S. Bhachu, G. Sankar and I. P. Parkin, *Chem. Mater.*, 2012, **24**, 4704.

10 (*a*) E. Guziewicz, M. Godlewski, T. Krajewski, Ł. Wachnicki, A. Szczepanik, K. Kopalko, A. Wójcik-Głodowska, E. Przeździecka, W. Paszkowicz, E. Łusakowska, P. Kruszewski, N. Huby, G. Tallarida and S. Ferrari, *J. Appl. Phys.*, 2009, **105**, 122413; (*b*) M. A. Thomas and J. B. Cui, *ACS Appl. Mater. Interfaces*, 2012, **4**, 3122.

11 K. Park, D.-K. Lee, B.-S. Kim, H. Jeon, N.-E. Lee, D. Whang, H.-J. Lee, Y. J. Kim and J.-H. Ahn, *Adv. Funct. Mater.*, 2010, **20**, 3577.

12 (*a*) H. C. Cheng, C. F. Chen and C. Y. Tsay, *Appl. Phys. Lett.*, 2007, **90**, 012113; (*b*) C. S. Li, Y. N. Li, Y. L. Wu, B. S. Ong and R. O. Loutfy, *J. Mater. Chem.*, 2009, **19**, 1626.

13 (*a*) J.-S. Lee, S.-M. Song, Y.-H. Kim, J.-Y. Kwon and M.-K. Han, *Phys. Status Solidi A*, 2013, 1–5; (*b*) M.-C. Chu, J. S. Meena, P.-T. Liu, H.-P. D. Shieh, H.-C. You, Y.-W. Tu, F.-C. Chang and F.-H. Ko, *Appl. Phys. Express*, 2013, **6**, 076501; (*c*) H. Faber, J. Hirschmann, M. Klaumünzer, B. Braunschweig, W. Peukert and M. Halik, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1693; (*d*) J. S. Meena, M.-C. Chu, S.-W. Kuo, F.-C. Chang and F.-H. Ko, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2582.

14 (*a*) S.-Y. Han, G. S. Harman and C.-H. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 5166; (*b*) R. Martins, E. Fortunato, P. Nunes, I. Ferreira, A. Marques, M. Bender, N. Katsarakis, V. Cimalla and G. Kiriakidis, *J. Appl. Phys.*, 2004, **96**, 1398.

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15 (*a*) P.-T. Liu, Y.-T. Chou and L.-F. Teng, *Appl. Phys. Lett.*, 2009, **95**, 233504; (*b*) P. P. Edwards, A. Porch, M. O. Jones, D. V. Morgan and R. M. Perks, *Dalton Trans.*, 2004, 2995; (*c*) T.-Y. Tseng and S. M. Sze, *Nonvolatile Memories: Materials, Devices and Applications*, American Scientific Publishers, Los Angeles, California, USA, 2012, vol. 1.
16 (*a*) R. Eason, *Pulsed Laser Deposition of Thin Films: Applications-LED Growth of Functional Materials*, Wiley-Interscience, A John Wiley & Sons, INC., Publications, New York, 2007; (*b*) M. S. Hammer, D. Rauh, V. Lorrmann, C. Deibel and V. Dyakonov, *Nanotechnology*, 2008, **19**, 485701.
17 V. A. Johnson and K. Lark-Horovitz, *Phys. Rev.*, 1953, **92**, 226.
18 J. Y. Lee, C. M. Shin, J. H. Heo, C. R. Kim, J. H. Park, T. M. Lee, H. Ryu, C. S. Son, B. C. Shin and W. J. Lee, *Current Applied Physics*, 2010, **10**, S290.
19 (*a*) M. Mekhnache, A. Drici, L. S. Hamideche, H. Benzarouk, A. Amara, L. Cattin, J. C. Bernede and M. Guerioune, *Superlattices Microstruct.*, 2011, **49**, 510; (*b*) Z. L. Pei, X. B. Zhang, G. P. Zhang, J. Gong, C. Sun, R. F. Huang and L. S. Wen, *Thin Solid Films*, 2006, **497**, 20.
20 P. K. Nayak, M. N. Hedhili, D. Cha and H. N. Alshareef, *Appl. Phys. Lett.*, 2012, **100**, 202106.
21 Z. Fan, D. Wang, P.-C. Chang, W.-Y. Tseng and J. G. Lu, *Appl. Phys. Lett.*, 2004, **85**, 5923.
22 (*a*) M.-G. Kim, H. S. Kim, Y.-G. Ha, J. He, M. G. Kanatzidis, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2010, **132**, 10352; (*b*) J. Xie, D. Xin, H. Cao, C. Wang, Y. Zhao, L. Yao, F. Ji and Y. Qiu, *Surf. Coat. Technol.*, 2011, **206**, 191; (*c*) K. Y. Rhee, S. J. Park, D. Hui and Y. Qiu, *Composites, Part B*, 2012, **43**, 2395.
23 (*a*) M. N. Kamalasanan and S. Chandra, *Thin Solid Films*, 1996, **288**, 112; (*b*) A. Kelchtermans, K. Elen, K. Schellens, B. Conings, H. Damm, H.-G. Boyen, J. D'Haen, P. Adriaensens, A. Hardy and M. K. Van Bael, *RSC Adv.*, 2013, **3**, 15254.
24 S. K. Sharma, A. I. Inamdar, H. Im, B. G. Kim and P. S. Patil, *J. Alloys Compd.*, 2011, **509**, 2127.
25 (*a*) C. Busch, G. Schierning, R. Theissmann and R. Schmechel, *J. Appl. Phys.*, 2012, **112**, 034506; (*b*) J. S. Meena, M.-C. Chu, C.-S. Wu, Y.-C. Chang, F.-C. Chang and F.-H. Ko, *Org. Electron.*, 2011, **12**, 1414; (*c*) L. Li, W. Hu, L. Chi and H. Fuchs, *J. Phys. Chem. B*, 2010, **114**, 5315.
26 I. Abdel-Motaleb, N. Shetty, K. Leedy and R. Cortez, *J. Appl. Phys.*, 2011, **109**, 014503.
27 C. G. Van de Walle, *Phys. Rev. Lett.*, 2000, **85**, 1012.
28 (*a*) B. S. Ong, C. Li, Y. Li, Y. Wu and R. Loutfy, *J. Am. Chem. Soc.*, 2007, **129**, 2750; (*b*) K. Song, J. Noh, T. Jun, Y. Jung, H.-Y. Kang and J. Moon, *Adv. Mater.*, 2010, **22**, 4308.
29 M. Liu and H. K. Kim, *Appl. Phys. Lett.*, 2004, **84**, 173.
30 C. W. Litton, D. C. Reynolds and T. C. Collins, *Zinc Oxide Materials for Electronic and Optoelectronic Device Applications*, Wiley, Chichester, UK, 2011.
31 S. Walther, S. Polster, M. P. M. Jank, H. Thiem, H. Ryssel and L. Frey, *Adv. Powder Technol.*, 2011, **22**, 253.

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