Spray-deposited Li-doped ZnO transistors with electron mobility exceeding 50 cm²/Vs

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The ever increasing demand for high performance electronic devices that can be fabricated onto large-area substrates employing low manufacturing cost techniques has given a boost to the development of alternative types of semiconductor materials, such as organics and metal oxides, with desirable physical characteristics that are absent in their traditional inorganic counterparts. Metal oxide semiconductors, in particular, are very attractive for implementation into thin-film transistors (TFTs)^[1-2] mainly because of their high charge

carrier mobility, high optical transparency, excellent chemical stability, mechanical stress tolerance and processing versatility^[3-5]. Oxide semiconductors are usually grown using vacuum-based techniques such as sputtering^[6-8], pulsed laser deposition^[9], chemical vapour deposition^[10], and ion-assisted deposition^[11-12]. Based on these methods, the synthesis of a wide range of metal oxide semiconductors with high charge carrier mobilities and low carrier concentration has been demonstrated^[7]. Many of these materials have been investigated for applications in thin-film electronics where transistors with electron mobilities up to 140 cm²/Vs have been demonstrated^[7,11-16]. Despite the great promise however, the application of vacuum-based technologies for the deposition of complex oxide semiconductors suffers from incompatibility with large-area substrates and hence high manufacturing cost. To this end, the development of alternative deposition methods based on solution processing paradigms could provide a breakthrough in both cost and performance by marrying fabrication simplicity with high-throughput manufacturing.

In recent years a wide variety of soluble precursors compounds have been examined as potential alternatives for the fabrication of oxide-based TFTs using large area deposition methods including spin casting, dip coating and spray pyrolysis. For example, metal oxides such as zinc oxide (ZnO)^[17-22], indium oxide (In₂O₃)^[23-24], indium gallium oxide (InGaO)^[25], indium zinc oxide (InZnO)^[18-26] and zinc tin oxide (ZnSnO)^[27] have been synthesised using soluble precursors and implemented into TFT structures. Despite the process simplicity, excellent charge carrier mobilities have been achieved, clearly demonstrating the significant potential of this alternative processing methodology. Here we show how spray pyrolysis (SP) can be used for the deposition of doped ZnO films and the fabrication of high electron mobility TFTs onto large area substrates under ambient atmosphere. Doping is achieved by simple physical blending of the soluble precursor compounds in water or alcohol based solutions. Among the various dopants studied, transistors fabricated using Li doped ZnO were

found to yield the best performance with maximum electron mobility $> 50 \text{ cm}^2/\text{Vs}$ and on/off current modulation ratio exceeding 10^6 .

Preparation of the Li doped precursor solutions is described in the *Experimental* section. Conversion of the precursor into Li-doped ZnO films is achieved by spray pyrolysis above 350°C . This was verified by FTIR measurements (data not shown). The microstructure and morphology of as-deposited Li-ZnO films were investigated by tapping-mode atomic force microscopy (AFM) and wide-angle X-ray scattering (WAXS). Figure 1 shows the phase and topography AFM micrographs for Li-doped ZnO films with Li to Zn molar ratio of 0 %, 1 % and 4 %. It can be seen that the ZnO grain size increases with increasing Li concentration (stoichiometry in solution) and reaches values close to the actual film thickness (30-40 nm) at higher Li content. Detailed microstructure analysis of the AFM micrographs yields average crystal sizes of 22 nm, 43 nm and 66 nm for $[\text{Li}^{+1}]/[\text{Zn}^{+2}]$ molar ratios of 0 %, 1 %, and 4 %, respectively. The film surface average roughness increases with increasing Li concentration up to 1% for which it reaches a maximum value of 12 nm. This increase is followed by a decrease for higher Li concentration (see Figure S1).

To assess the effects of the morphology evolution on the electronic characteristics of Li-doped ZnO films, a series of thin-film transistors with varying channel geometries have been fabricated. The actual transistor channel dimensions have been measured using a scanning electron microscope (SEM). Figure 2a and 2b displays typical sets of the transfer and output characteristics, respectively, for TFTs based on Li-doped ZnO films deposited at 400°C using a $[\text{Li}^{+1}]/[\text{Zn}^{+2}]$ molar ratio of 1 % in methanol solution. The transistors exhibit on/off current ratio in the range 10^6 - 10^7 , negligible operating hysteresis and threshold voltages (V_T) in the range 20-30 V. The electron injecting aluminium S-D electrodes used here are found to form Ohmic-like contact with the conducting band of Li-ZnO as evident by

the linearity of the output curves at low drain voltages (V_D). The maximum electron mobility calculated from these transistors is of the order of $54 \text{ cm}^2/\text{Vs}$. We note that despite the early stage of optimisation for spray pyrolysis, the obtained electron mobility is nearly 50% higher than the previous record value obtained from solution deposited oxide TFTs.^[28]

One interesting observation is that short channel ($<30 \text{ }\mu\text{m}$) Li-ZnO TFTs show higher electron mobilities as compared to long channel devices ($>20 \text{ }\mu\text{m}$). The effect is attributed to grain boundary limited electron transport^[21,29]. This effect is better illustrated in Figure 2c where the saturated electron mobility, obtained from a number (e.g. 8-10) of Li-doped ZnO TFTs, is plotted as a function of Li doping (solution stoichiometry) and transistor channel length. The same trend is observed for the linear mobility in these TFTs as well as in Li-doped ZnO transistors based on bottom-gate, bottom-contact (BG-BC) utilising gold source-drain electrodes. An important implication of this observation is that the charge mobility could in principle be further enhanced, within limits, by simply decreasing the channel length of the transistor to $< 20 \text{ }\mu\text{m}$. We note however that in the case of bottom-gate bottom-contact ZnO TFTs employing gold source-drain electrodes, the mobility exhibits a maximum around $L \sim 5 \text{ }\mu\text{m}$ and reduces at shorter channel lengths (i.e. $<5 \text{ }\mu\text{m}$). Therefore downscaling of L as a mean of enhancing the electron mobility is effective only down to a critical length.

In order to gain a better understanding of the dependence of carrier mobility on Li-doping, we performed WAXS experiments on as-deposited films. Figure 3a displays the WAXS patterns of the undoped and doped ZnO films for different Li doping levels. As reference, the WAXS pattern of a commercially available ZnO nanopowder (grain size $< 100 \text{ nm}$) is also shown. All diffraction peaks can be indexed to the (002) and (103) planes of reflection of a hexagonal wurtzite ZnO structure, indicating a polycrystalline nature of the films^[30]. It is to be noted that for the entire Li doping range, no peak for Li-related compound

could be identified, indicating that the crystalline parts of the Li-doped films consist of the pure ZnO phase only. Additionally, the peak intensity at 34.6 degrees indicates that the spray pyrolysed films are highly textured, with the crystalline domains being preferentially oriented along the (002) direction. Figure 3b illustrates the average crystal size extracted using the Scherrer formula^[31] utilising both the (002) and (103) diffraction peaks. The lattice parameters a, c and u for the optimum Li doping concentration were found to be 3.263 Å, 5.193 Å and 0.381 c units respectively. The evolution of the lattice parameters a, c, u as well as the interplanar spacing d_{HKL} for varying the Li content are shown in Figures S2 and S3 respectively. This trend denotes the enlargement of the ZnO crystal size for the optimum $[\text{Li}^{+1}]/[\text{Zn}^{+2}]$ molar ratio, i.e. 1%. It must be noted that given the absence of any features at about 48.9 degrees from the WAXS patterns, we can safely eliminate the possibility of the co-existence of any Li_2O compounds in our films even for the higher Li concentration.

The Li-doped ZnO films were also investigated using photoluminescence (PL) spectroscopy (Figure S4). As deposited films show a strong emission peak at around 378 nm (UV emission) due to the excitonic transition and a broad band in the range of 420–600 nm (“green” emission). From these measurements it can be concluded that Li doping of up to 1 % enhances the concentration of defects that act as radiative paths and are responsible for the visible luminescence. This enhances broadening and intensity of the “green” emission. For higher Li concentrations both the UV emissions and green are diminished, indicating that a high Li doping probably leads to the formation of complex defects which are responsible for the quenching of the visible emission^[32].

Figure 3c shows that the optical transmittance decreases sharply below 400 nm for all ZnO films. Although, the excitonic absorption peak is present for all Li-doped ZnO films, it is particularly prominent in films with doping concentration (i.e. $[\text{Li}^{+1}]/[\text{Zn}^{+2}]$) around 1 %. The

broadening of the peak and the onset of an additional absorption feature at about 490 nm for the film with the optimum Li doping level is assigned to the formation of defect sites, discussed above, that are responsible for the degradation of the optical quality of the films. This finding is consistent with the evolution of the optical band gap (Figure S5) where a minimum value for the optimal Li doping concentration is observed. The optical band gap has also been calculated using spectroscopic ellipsometry (SE) measurements at the spectral region from 1.5 to 4.5 eV.^[21] Figures S5 and S6 provide further details on the evolution of the infinite refractive index and voids used in the modelling as well as the real, imaginary dielectric function parts and reflection dispersions for the film that shows the highest field effect mobility. They are all consistent with the trends reported above.

In summary we have demonstrated solution processed Li-doped ZnO transistors with maximum electron mobility of 54 cm²/Vs. The physical properties of Li-ZnO films have been investigated using a range of characterisation techniques. Structural studies show that Li doping can lead to either interstitial or substitutional doping depending on the doping level. Interstitial doping was observed for Li concentration $\leq 1\%$ and found to yield the best TFTs with maximum electron mobility >50 cm²/Vs. For doping concentration $>1\%$ it was shown that substitutional doping of Zn by Li occurs resulting to a drastic reduction in the average crystal size and interplanar spacing accompanied by a significant reduction in the electron mobility.

The use of spray pyrolysis for the deposition of metal oxides described here expands the possibilities for the development of improved multi-component oxide semiconductors that can be processed onto large area substrates using this rather simple and low manufacturing cost deposition process. A remarkable aspect of our approach is the accurate control over the electronic properties of the spray deposited films through simple physical blending of

precursor solutions and soluble dopant molecules, clearly demonstrating the potential for the rapid development of oxide semiconductors far beyond those accessible by traditional deposition methods.

Experimental

ZnO Deposition by Spray Pyrolysis: A 0.1 M solution of zinc acetate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2$) and a 0.1 M solution of lithium acetate dihydrate ($\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$) was prepared in methanol. The desired amount of the parent Li acetate solution was then added into the parent solution of Zn acetate to obtain the desired mass ratio (i.e. doping level). The substrates were kept at 400 °C on a hotplate, while aerosols of the solution were sprayed intermittently onto the substrates employing a conventional airbrush, held at a vertical distance of 20–30cm. After a period of 15 s, the spraying process was interrupted for 60 s to allow for the vapour to settle onto the sample before the cycle was repeated until films of typical thicknesses of 35 nm were obtained.

Transistor Fabrication: Bottom-gate, top-contact (BG-TC) transistors were fabricated on heavily doped silicon (Si^-) wafers employing a SiO_2 gate dielectric 400 nm thick. Aluminium (Al) source/drain electrodes were thermally evaporated under high vacuum (10^{-6} mbar) through a shadow mask following the deposition of ZnO films by SP.

Transistor Characterization: Device characterization was performed under high vacuum (10^{-5} mbar) at room temperature. Electrical measurements were carried out using an Keithley 4200 Semiconductor Parameter Analyzer. Electron mobility was extracted from the transfer curves in the saturation regime using the gradual channel approximation:

$$\mu_{e,sat} = \frac{L}{C_i W} \frac{\partial^2 I_D}{\partial V_G^2} \quad (1)$$

$$\mu_{e,lin} = \frac{L}{C_i W V_D} \frac{\partial I_D}{\partial V_G} \quad (2)$$

where, C_i is the geometrical capacitance of the dielectric layer and L and W the length and width of the transistor channel, respectively.

AFM measurements: Atomic force micrographs of the oxide films deposited onto Si/SiO₂ were taken in tapping mode using a Veeco Dimension 3100 SPM.

Wide-angle X-ray scattering: Wide-angle X-ray scattering (WAXS) experiments were performed on doped and neat ZnO films that were deposited on corning glass substrates using a Phillips PW 1050/25 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) operating at 30 KV.

Photoluminescence spectroscopy: Li-doped ZnO films on c-Si were excited with the 340 nm line of Xenon Arc Lamp and the PL spectra were recorded using FluoroMax-3 system by Horiba Jobin Yvon at the spectral range from 350 to 600 nm.

UV-Vis absorption spectroscopy: Optical absorption of the Li-doped ZnO films on quartz substrates was measured at wavelengths between 190 and 1000 nm using a UV-Vis Shimadzu 2550 spectrometer at the dual beam mode.

Spectroscopic Ellipsometry (SE): SE measurements of Li-doped ZnO films on SiO₂ and c-Si were performed in ambient conditions at an incidence angle of 70° using a Jobin-Yvon UVISSEL phase modulated system.

FTIR: The FTIR measurements of Li-doped ZnO films on Caesium Iodine (CsI) substrates were conducted in transmission mode using a Perkin Elmer system 2000 Fourier transform spectrophotometer at the spectral ranges from 6000-370 cm⁻¹ (KBr beam splitter), and 700 cm⁻¹ to 200 cm⁻¹ (polystyrene beam splitter) at a spectral resolution of 1 cm⁻¹.

Raman spectroscopy: Unpolarised visible Raman spectra of Li-doped ZnO films on CsI were excited at the backscattering geometry using the 488 nm line of an Ar⁺ laser. Fused silica optics were used throughout and the spectra were collected on a charge-coupled device

camera using a Renishaw micro Raman system 1000 spectrometer. A laser output of 15 mW was used, which resulted in an incident power at the sample of <1 mW.

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Figures

Figure 1: AFM micrographs of Li-doped ZnO. Phase and topography micrographs of Li-doped ZnO films on SiO₂ for $[\text{Li}^{+1}]/[\text{Zn}^{+2}]$ of 0 %, 1 % and 4% (molar ratio in precursor solution) are shown.

Figure 2: Thing film transistor (TFT) characteristics of Li-doped ZnO. **a.** Linear ($V_D = 2$ V) and saturated ($V_D = 40$ V) transfer characteristics of bottom-gate, top-contact TFTs with channel width $W = 1000$ μm and channel length $L = 20$ μm , fabricated with ZnO films of optimum $[\text{Li}^+]/[\text{Zn}^{+2}] = 1$ % molar ratio. **b.** Output characteristics of the same TFT. Inset of figure 2a shows the bottom-gate, top-contact TFT architecture employed. **c.** Contour plot (isopleth) of the field-effect electron mobility as a function of channel length (L) and the $[\text{Li}^+]/[\text{Zn}^{+2}]$ molar ratio.

Figure 3: Wide-angle X-ray scattering data (WAXS) of Li-doped ZnO. **a.** WAXS patterns of Li-doped ZnO films of varying $[\text{Li}^+]/[\text{Zn}^{+2}]$ molar ratio (solution stoichiometry), deposited on corning glass. A reference WAXS pattern of nanopowder ZnO (grain size < 100 nm) is also included. **b.** Average crystal size of such Li-doped ZnO films. The crystal size values were derived from both (002) and (103) diffraction peaks by the application of the Scherrer formula assuming a shape factor of 0.95. **c.** Transmittance (%) spectra of Li-doped ZnO films deposited at 400 °C on quartz substrates for $[\text{Li}^+]/[\text{Zn}^{+2}]$ molar ratios in the range 0-4 %.

Supporting Information

Figure S1: Average and rms roughness of Li-doped ZnO on SiO₂.

Figure S2: Lattice parameters a , c and u of Li-doped ZnO based on wurtzite structure for varying the Li doping level.

Figure S3: Interplanar (002) and (103) spacing d_{HKL} of Li-doped ZnO films.

Figure S4. a. PL spectra of Li-doped ZnO thin films of $[Li^{+1}]/[Zn^{+2}]$ molar ratios between 0 and 4 %, deposited on Si substrates. The films were excited with the 340 nm line of a Xenon Arc Lamp and the PL spectra were recorded at the spectral range from 350 nm to 600 nm b. "Green" to "UV" emission peaks area ratio (left y-axis) and FWHM of the "green emission" peak that illustrates its broadening for varying the Li doping level.

Figure S5: Li-doped ZnO infinite refractive index n_{∞} and voids in structural model derived form for SE data analysis.

Figure S6: Reflectance, imaginary and real part of dielectric function of Li-doped ZnO for the optimum $[\text{Li}^{+1}]/[\text{Zn}^{+2}]$ molar ratio of 1 %.