Durham Research Online

Deposited in DRO:
17 January 2018

Version of attached file:
Published Version

Peer-review status of attached file:
Peer-reviewed

Citation for published item:

Further information on publisher’s website:
https://doi.org/10.1063/1.4968194

Publisher’s copyright statement:

Additional information:

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:
- a full bibliographic reference is made to the original source
- a link is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the full DRO policy for further details.
Atomic layer deposition of Nb-doped ZnO for thin film transistors
A. Shaw, J. S. Wrench, J. D. Jin, T. J. Whittles, I. Z. Mitrovic, M. Raja, V. R. Dhanak, P. R. Chalker, and S. Hall

Citation: Appl. Phys. Lett. 109, 222103 (2016);
View online: https://doi.org/10.1063/1.4968194
View Table of Contents: http://aip.scitation.org/toc/apl/109/22
Published by the American Institute of Physics

Articles you may be interested in

High performance thin film transistor (flex-TFT) with textured nanostructure ZnO film channel fabricated by exploiting electric double layer gate insulator

Silicon induced stability and mobility of indium zinc oxide based bilayer thin film transistors

Demonstration of flexible thin film transistors with GaN channels

Compositional tuning of atomic layer deposited MgZnO for thin film transistors

Metal oxide semiconductor thin-film transistors for flexible electronics
Applied Physics Reviews 3, 021303 (2016); 10.1063/1.4953034

High-performance staggered top-gate thin-film transistors with hybrid-phase microstructural ITO-stabilized ZnO channels
Atomic layer deposition of Nb-doped ZnO for thin film transistors

A. Shaw,¹ J. S. Wrench,² J. D. Jin,¹ T. J. Whittles,³ I. Z. Mitrovic,¹ M. Raja,¹ V. R. Dhanak,³ P. R. Chalker,² and S. Hall¹*(a)

¹Department of Electrical and Electronic Engineering, University of Liverpool, Liverpool L69 3GJ, United Kingdom
²School of Engineering, Centre for Materials and Structures, University of Liverpool, Liverpool L69 3GH, United Kingdom
³Department of Physics and Stephenson Institute of Renewable Energy, University of Liverpool, Liverpool L69 3BJ, United Kingdom

(Received 12 August 2016; accepted 6 November 2016; published online 29 November 2016)

We present physical and electrical characterization of niobium-doped zinc oxide (NbZnO) for thin film transistor (TFT) applications. The NbZnO films were deposited using atomic layer deposition. X-ray diffraction measurements indicate that the crystallinity of the NbZnO films reduces with an increase in the Nb content and lower deposition temperature. It was confirmed using X-ray photoelectron spectroscopy that Nb5⁺ is present within the NbZnO matrix. Furthermore, photoluminescence indicates that the band gap of the ZnO increases with a higher Nb content, which is explained by the Burstein-Moss effect. For TFT applications, a growth temperature of 175 °C for 3.8% NbZnO provided the best TFT characteristics with a saturation mobility of 7.9 cm²/Vs, the current On/Off ratio of 1 x 10⁸, and the subthreshold swing of 0.34 V/decade. The transport is seen to follow a multiple-trap and release mechanism at lower gate voltages and percolation thereafter.

Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4968194]

Zinc oxide (ZnO) has received a great deal of attention over the recent years particularly for the application of transparent electronics for active matrix displays. ZnO shows advantages when compared to materials such as amorphous silicon in terms of higher saturation mobilities¹,² and a larger band gap (Eg ~ 3.37 eV)³ enabling the potential for transparent display technology. The atomic layer deposition (ALD) of ZnO provides the potential for large area homogeneous films. Low temperature ALD (<150 °C) is known to achieve the best performance as the films are less conductive, with the reported mobilities of >10 cm²/Vs.³-⁵ However, indium gallium zinc oxide (IGZO) is the preferred ZnO based material for thin film transistors (TFTs)⁶ due to its relatively high electron mobility, stability, and good control of conductivity.

However, for large scale production, non-indium based materials are desirable for cost effectiveness, hence the requirement for alternative dopants. Research into non-indium based ZnO materials for TFT application includes: gallium,⁷ silicon,⁸ and magnesium.⁹ These dopants act as effective oxygen vacancy (Vo) suppressors and can further increase the band-gap of the ZnO through the Burstein-Moss effect.⁷-⁹ Niobium (Nb) has the potential as a dopant, due to its high valency (Nb5⁺) which offers the prospect of a Vo suppressor, superior to the dopants gallium (Ga3⁺), silicon (Si4⁺), and magnesium (Mg2⁺). Furthermore, Nb can act as an effective substitutional dopant for Zn2⁺ and subsequently reduce the disorder and carrier scattering. To date, the studies of Nb-doped ZnO (NbZnO) films have been reported using pulse layer deposition (PLD)¹⁰,¹¹ and sputtering.¹² The use of Nb-doping in transparent semiconducting oxides has been reported for TiOx TFTs.¹³ In this letter, we present the physical and electrical characteristics of NbZnO films for active layers in TFT applications.

The NbZnO films of nominal thickness 50 nm were deposited using ALD on heavily doped, thermally oxidized (50 nm) n-type Si wafers. A capping layer of 5 nm Al₂O₃ was first deposited by ALD at 200 °C on the SiO₂. The active layer NbZnO was then deposited at 200 °C using the precursors diethlyzinc (DEZn) and niobium pentaethoxide (Nb(OEt)₅); temperatures of these precursors entering the chamber were ambient and 140 °C, respectively. The Nb ALD cycle fraction was varied from 1% to 12.5%, where the NbZnO films were made by first depositing the x-cycles of ZnO by successive steps of DEZn and then H₂O vapor on the surface. After the x-cycles of ZnO, a single Nb₂O₅ cycle is deposited by the successive steps of Nb(OEt)₅ and H₂O. The process is repeated until the desired film thickness is reached. For example, a film with a Nb cycle percentage of 2% would be achieved by 49 cycles of DEZn and H₂O (x = 49) followed by 1 cycle of Nb(OEt)₅ and H₂O repeated 6 times giving a total of 294 ZnO and 6 Nb₂O₅ cycles. This equates to a cycle fraction of 0.02 and a cycle percentage of 2% (6/(294 + 6) x 100% = 2%). The thickness of the films was confirmed by spectroscopic ellipsometry as 52 ± 2 nm. The effect of the ALD growth temperature was tested for 3.8% NbZnO at 150, 175, 200, and 225 °C.

X-ray diffraction (XRD), photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS) were performed to determine the crystallographic nature, optical properties, and composition, respectively. The XRD measurements were performed on 1% NbZnO as-deposited, 1% to 12.5% NbZnO annealed for 1 hour at 300 °C air, and 3.8% NbZnO grown at 150 °C, 200 °C, and 225 °C annealed under the same conditions. The crystalline phases were identified by XRD using Cu Kα radiation (0.154051 nm, 40 kV, and 50 mA), and the

*(a)Author to whom correspondence should be addressed. Electronic mail: S.Hall@liverpool.ac.uk

003-6951/2016/109(22)/222103/4/$30.00 109, 222103-1 Published by AIP Publishing.
Diffraction patterns are shown in Figs. 1(a) and 1(b). The films are polycrystalline with peaks (100), (002), and (101). Fig. 1(a) shows the comparison between a 1% NbZnO film as-grown at 200°C and after annealing. The act of annealing in air enhances the film crystallinity as indicated by the increase in the intensity of the (100) and (101) peaks as well as the reduction of their full width at half maxima (FWHM) from 0.50 to 0.45 and 0.51 to 0.44, respectively. In general, there is greater (002) directionality, although as the Nb content is increased, the films’ crystallinity is reduced eventually becoming amorphous at 9.1% and above. For the (002) peak, the grain size is reduced from 20 to 14 nm and an increase in Nb from 1% to 6.8% is calculated using the Scherrer equation. This reduction in ZnO crystallinity with Nb concentration has also been reported when grown using PLD. Fig. 1(b) demonstrates that reducing the growth temperature serves to reduce the crystallinity of the ZnO as there are no observable (002) or (101) peaks at 150°C.

The PL measurements were performed using a 325 nm (3.82 eV) He-Cd laser and a Raman confocal microscope set to 100 μm aperture coupled to a single grating spectrometer equipped with a notch filter and a CCD camera detector. The PL spectrum of the as-deposited samples with varying Nb content is shown in Fig. 1(c). As the Nb cycle percentage is increased, the band edge increases to 3.58 eV, consistent with spectroscopic ellipsometry results. This increase can be described by the Burstein-Moss effect; similar band energy shifts have been reported for NbZnO prepared by PLD, spray pyrolysis, and electrostatic spray deposition.

The core level (CL) structure and the occupied density of states in the valence band were probed by XPS; further experimental details of which can be found elsewhere. For the XPS measurements, 10 nm films were used, which correspond to the nominal surface sensitivity of the technique. Core level peak energies were corrected using adventitious carbon C 1s peak at 284.6 eV for all samples. The CL spectra for the Nb 3d5/2 and Zn 2p3/2, O 1s for bulk ZnO, 3.8% and 12.5% NbZnO grown at 200°C are shown in Fig. 2. Fig. 2(a) shows that the Nb 3d5/2 peak for bulk Nb2O5 has a binding energy (BE) of 207.1 eV indicating the presence of Nb5+. For 3.8% and 12.5% NbZnO, the Nb 3d5/2 peak shifts to a lower BE of 206.8 eV. Conversely, Fig. 2(b) indicates an increase in the BE for the Zn 2p3/2 peak, from 1020.1 eV for bulk ZnO to 1021.2 eV and 1021.3 eV for 3.8% and 12.5% NbZnO, respectively. This implies that Nb5+ species are present in the film as a substitutional dopant due to the nature of the charge transfer. Fig. 2(c) indicates that for bulk ZnO, the O 1s CL shows 3 sub-peaks relating to (i) the oxygen atoms bonded with the nearest neighbor metal ion species (Zn-O), (ii) the oxygen atoms in the vicinity of an oxygen vacancy (labelled as O2− deficiency peak), and (iii) surface oxygen such as O-C-O or hydroxyl groups. Furthermore, 3.8 and
12.5% NbZnO has these sub-peaks with the addition of a sub-peak with a BE of 530.5 eV, which we assign to the presence of an Nb-O environment confirmed by the O 1s Nb2O5 peak (see supplementary material). It is evident that the O 1s CL shifts to higher binding energies with the addition of Nb from 529.5 eV to 529.9 eV as a consequence of Nb5+ species present within the film. Furthermore, it is evident that there is an increase of O2− deficiencies with an increase in Nb5+, shown by the increased sub-peak at 531.4 eV.20,21 Moreover, the oxygen vacancies can be reduced by annealing in an oxy- gen rich environment (see supplementary material). The improved μsat is considered to be due to the high oxidation state of Nb5+. Table I indicates that the On/Off ratio decreases with an increase ingrowth temperature for 3.8% NbZnO, together with a positive shift in VGS. Furthermore, μsat stays about the same for temperatures above 175 °C. The lower mobility for 150 °C NbZnO can be attributed to the reduced crystallinity apparent from Fig. 1(b).

More appropriate physical modelling of the TFTs is achieved by considering a power law dependency of current on gate voltage, which arises by considering an exponential density of electron states (DoS) in the material.22 The drain current mechanism is then described by the multi-trapping and release (MTR) model

\[ I_{DS} = \frac{W}{L} \beta \left[ (V_{GS} - V_{FB} - (I_{DSRS})^\gamma)^{1/\gamma} - (V_{GS} - V_{FB} - (I_{DDS})^\gamma)^{1/\gamma} \right] \]

(2)

The power law index is defined as \( \gamma = T_o / T \), where \( T_o \) is a characteristic temperature related to the exponential DoS;22

\[ V_{FB} \] is the flat band voltage, \( \beta \) is a transconductance parameter, 

Moreover, small Nb cycle percentages serve to increase the on-current; however, the increased Nb concentration reduces the films’ conductivity, indicated by the change in \( \mu_{sat} \).15

Table I shows the extracted parameters for different growth temperatures, together with pure ZnO and 12.5% NbZnO for the purpose of comparison. Typical TFT output and transfer characteristics are shown in Figs. 3(a) and 3(b), respectively, for the 3.8% NbZnO film grown at 175 °C, where the symbols designate measured characteristics.

Comparing the different Nb cycle percentages in Table I, it is evident that Nb serves to increase the On/Off ratio by reducing the off-current.15 The On/Off ratio is defined as the maximum current and when the TFT begins to conduct.

**TABLE I.** TFT characteristics for the 3.8% NbZnO growth temperature study and comparison with pure ZnO and 12.5% NbZnO showing the average of 5 measured devices.

<table>
<thead>
<tr>
<th>Nb cycle (%)</th>
<th>Temp. (°C)</th>
<th>On/Off ratio</th>
<th>V_T (V)</th>
<th>( \mu_{sat} ) (cm²/Vs)</th>
<th>SS (mV/dec)</th>
<th>V_FB (V)</th>
<th>T_o (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0^15</td>
<td>200</td>
<td>1 x 10⁶</td>
<td>9.3 ± 1.0</td>
<td>1.4 ± 0.2</td>
<td>2970 ± 300</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>3.8</td>
<td>150</td>
<td>3 x 10⁶</td>
<td>7.9 ± 0.2</td>
<td>4.8 ± 0.1</td>
<td>220 ± 20</td>
<td>-4.0</td>
<td>539</td>
</tr>
<tr>
<td>175</td>
<td>1 x 10⁶</td>
<td>8.5 ± 0.1</td>
<td>7.9 ± 0.1</td>
<td>340 ± 40</td>
<td>-1.5</td>
<td>541</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>1 x 10⁷</td>
<td>9.3 ± 0.1</td>
<td>7.9 ± 0.1</td>
<td>470 ± 30</td>
<td>-3.3</td>
<td>570</td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>9 x 10⁶</td>
<td>9.8 ± 0.1</td>
<td>7.0 ± 0.1</td>
<td>870 ± 20</td>
<td>-1.2</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>12.5^15</td>
<td>200</td>
<td>1 x 10⁷</td>
<td>1.0 ± 1.0</td>
<td>0.1 ± 0.1</td>
<td>1080 ± 200</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

and $R_S$ and $R_D$ are the source and drain series resistances, respectively. Fitting of (2) with experimental data was performed by linear regression with a regression coefficient, $R^2$, of 0.99 and 0.93 for the transfer and output characteristics, respectively. Fits for the 175°C NbZnO TFT are shown in Fig. 3. The power dependency of $I_{DS}$ increased from 3.6 to 4.13 with temperature and the corresponding $T_o$, as shown in Table I. It can be seen that $T_o$ and $SS$ are correlated and is representative of the degree of disorder in the film, which translates into a poorer $SS$. Comparing the TFT performance with our similar work on Mg doping, the lower $T_o$ and $SS$ indicate that Nb is a more effective dopant for ZnO. Furthermore, it has been reported for metal oxide semiconductors that for sufficiently large $V_{GS}$, a mechanism of percolation dominates the current transport. Following the analysis outlined in Refs. 24 and 25, the TFTs are seen to follow a similar transport physics with the onset of percolation current ($E_F = E_C$) at $V_{GS} \approx 15$ V for 175°C NbZnO. The associated effective density of tail states was found to be $1.5 \times 10^{18}$ cm$^{-3}$.

In conclusion, ALD has been used to deposit NbZnO films for TFT applications. It has been established from XPS that Nb$^{5+}$ exists within the NbZnO matrix. Furthermore, XRD indicates that NbZnO films are polycrystalline with low Nb cycle percentages over a range of growth temperatures. However, as the Nb cycle percentage increases, the films become amorphous while shifting the band gap to higher energies. Optimum TFT performance was achieved with 175°C 3.8% NbZnO where the $\mu_{sat}$ is superior to ALD ZnO doped with Mg$^9$ and Si.$^8$

See supplementary material for XPS CL spectra of bulk Nb$_2$O$_3$ O 1s and the effects of annealing in air on 12.5% NbZnO O 1s.

The authors thank the Engineering and Physical Sciences Research Council (EPSRC) for funding this project under Grant No. EP/K018884/1. V.R.D. acknowledges the support through the EPSRC Capital for Great Technologies—Grid Scale Energy Storage Programme; T.J.W. acknowledges funding through the EPSRC (Grant No. EP/J500471/1); the authors thank David Hesp for help with the XPS measurements.