Effects of Mg on the electrical characteristics and thermal stability of $Mg_xZn_{1-x}O$ thin film transistors

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The effects of the Mg composition (x=0, 0.06, and 0.10) on the electrical characteristics and thermal stability of $Mg_xZn_{1-x}O$ thin film transistors (TFTs) are investigated. The $Mg_{0.06}Zn_{0.94}O$ TFT shows the smallest subthreshold slope and highest field effect mobility. The O_{1s} spectra of x-ray photoelectron spectroscopy measurements indicate that the oxygen vacancies are reduced in $Mg_{0.06}Zn_{0.94}O$ relative to a pure ZnO channel device. $Mg_{0.06}Zn_{0.94}O$ TFTs also show higher thermal stability compared to the pure ZnO TFTs, which is mainly attributed to the suppression of oxygen vacancies in the channel. © *2011 American Institute of Physics*. [doi:10.1063/1.3567533]

Recently, ZnO thin film transistors (TFTs) have attracted increasing attention due to their high electron mobility, transparency to visible light, and superior radiation hardness. ZnO TFTs are potentially much less expensive than indium tin oxide based TFTs due to materials costs. It has been found that in ZnO based TFTs, the device characteristics, including field effect mobility, on-off ratio, subthreshold swing, and bias stress stability, are strongly impacted by the presence of native defects in the channel layer.[1] First principles calculation shows that the oxygen vacancy in ZnO has the lowest formation energy among the donorlike defects with deep electronic states.[2] Generally, an oxygen vacancy in the n-type ZnO is in the neutral state (V_o). However, under the negative gate voltage, the band bending can create the electron depletion region in the TFT channel. In this region, V_o can be excited to doubly the ionized state (V_o^{2+}) and releases electrons into the conduction band.[3] Thus, generation of V_o^{2+} from thermally excited V_o in the depletion region under a negative gate voltage increases the conductivity, resulting in the thermal instability of ZnO TFTs.

It has been reported that the incorporation of Mg into HfO_2 effectively reduces oxygen vacancies.[4] Current understanding is that Mg becomes strongly bonded to oxygen vacancies (V_o^{2+}) in HfO_2, neutralizing this defect. We speculate that the incorporation of certain metal ions (M) that have a stronger oxygen affinity than Zn in ZnO may also suppress the oxygen vacancies since the formation energy of oxygen vacancies depends in part on the M-O/Zn-O bonding energy. Mg might be a good candidate to serve as the oxygen vacancy suppressor in ZnO TFTs. First, the Mg^{2+} substitution in the Zn^{2+} site does not cause significant lattice distortion due to their similar ionic radii (Mg^{2+}:0.57 Å versus Zn^{2+}:0.60 Å). Second, owing to the strong ionic characteristic of MgO, the bonding energy of MgO (393.7 kJ/mole) is higher than ZnO (284.1 kJ/mol) at 298 K.[5] First principles calculations also indicates that MgO has a higher formation energy per oxygen vacancy (10.08 eV) than ZnO (7.01 eV).[6] It has been reported that alloying of Mg into ZnO can reduce deep level luminescence associated with oxygen vacancies in both polycrystalline and epitaxial $Mg_xZn_{1-x}O$ films.[7,8] However, there has been little information on use of Mg alloying in ZnO to form $Mg_xZn_{1-x}O$ TFTs.

Ohtomo *et al.*[9] studied the photoresponse of $Mg_xZn_{1-x}O$ TFTs (x=0, 0.1, and 0.3). The field effect mobility was found to decrease from 2.7 $cm^2/V\,s$ for ZnO to 0.8 $cm^2/V\,s$ for $Mg_{0.1}Zn_{0.9}O$ although no obvious structure change was found from x-ray diffraction. The degradation of the field effect mobility was attributed to the alloying disorder and increased effective mass of electrons.[9,10] Recently, Kim *et al.*[11] investigated how Mg alloying affects the bias stress stability of high indium content (molar ratio In:Zn =9:1) sol-gel InZnO (IZO) TFTs with increasing Mg/(In +Zn) ratios up to 0.4. The improvement of the bias stress stability, resulting from incorporation of Mg into the IZO TFTs, was attributed to smoother surface morphology, a reduced size of voids both at the interface and in the film, and enlargement of the band gap.

In this letter, we investigate the effects of Mg alloying on the electrical characteristics and thermal stability of $Mg_xZn_{1-x}O$ TFTs ($x \leq 0.1$). Mg^{2+} ions were incorporated to prevent oxygen out-diffusion and hinder the formation of oxygen vacancies in the TFT channel. The Mg composition is limited to no more than 10% to minimize deterioration of the field effect mobility. Bottom gate $Mg_xZn_{1-x}O$ TFTs were fabricated on heavily doped n-type Si wafers with a 100 nm thermally grown SiO_2. The 50 nm $Mg_xZn_{1-x}O$ (x=0, 0.06, and 0.10) channels are grown by metal-organic chemical vapor deposition at 450 °C. DEZn (diethyl zinc) and MCp_2Mg [bis (methylcyclopentadienyl) magnesium] are the precursors for Zn and Mg, respectively. The source and drain metallizations are formed with 100 nm Ti/50 nm Au by a lift-off process. The active layer is fixed at a width/length (W/L) =150 μm/5 μm. To prevent ambient absorption/desorption during the electrical testing, a SU-8 resist is coated on top of the TFT channel, serving as a passivation layer.[12] All the electrical tests are conducted in the dark using an HP-4156C electrical testing system with a temperature controlled chuck.

Figures 1(a) and 1(b) show the I_{DS}-V_{GS} characteristics in the linear and saturation regions for three TFTs with different

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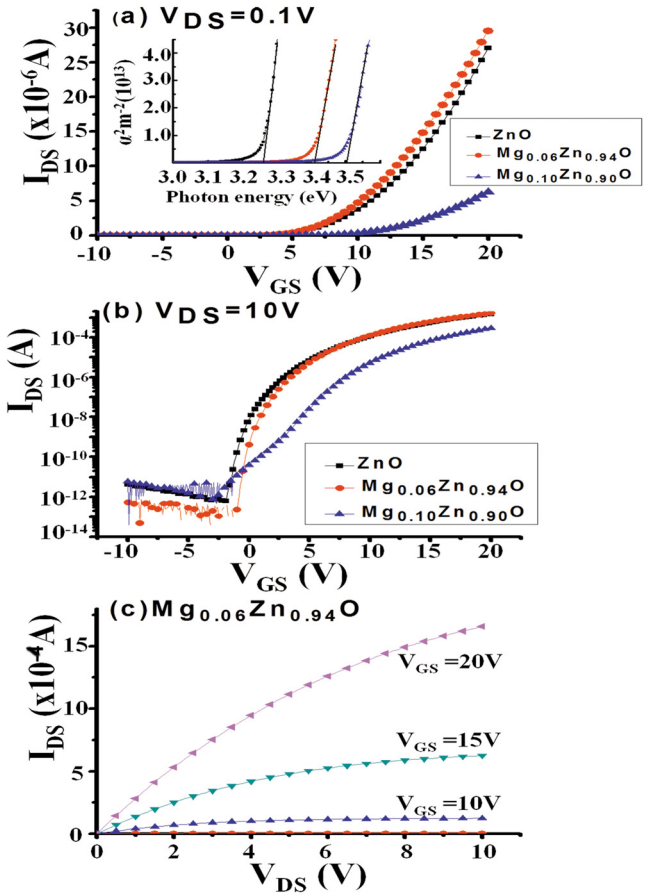

FIG. 1. (Color online) I_{DS}-V_{GS} transfer characteristics of ZnO, $Mg_{0.06}Zn_{0.94}O$, and $Mg_{0.1}Zn_{0.9}O$ TFTs: (a) in the linear region; the inset shows the α^2 vs $h\nu$ curves of ZnO, $Mg_{0.06}Zn_{0.94}O$ and $Mg_{0.1}Zn_{0.9}O$; (b) in the saturation region; and (c) the I_{DS}-V_{DS} characteristics of $Mg_{0.06}Zn_{0.94}O$ TFTs.

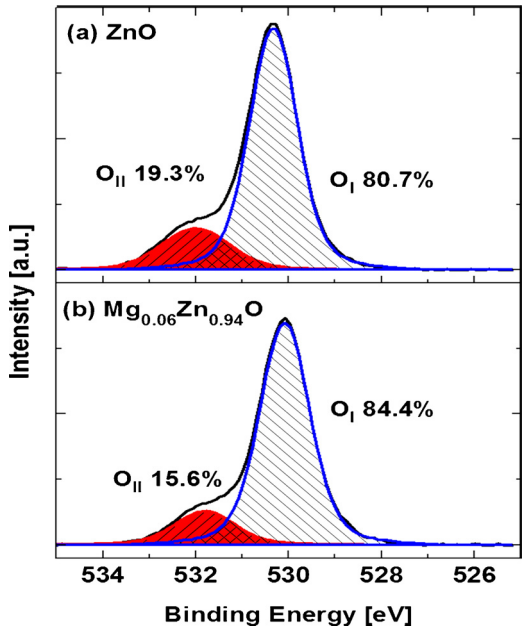

FIG. 2. (Color online) The O_{1s} peaks in the XPS spectra of (a) pure ZnO and (b) $Mg_{0.06}Zn_{0.94}O$ channel layers. The original O_{1s} peaks were deconvoluted by Gaussain fitting into two subpeaks including O_I (oxygen bonded with Zn) and O_{II} (oxygen vacancy related). The peak area of $O_{II}/(O_I+O_{II})$ is reduced after incorporation of 6% Mg into the ZnO.

Mg concentrations. The Mg composition values x in the $Mg_xZn_{1-x}O$ are extracted from the absorption curves (α^2 versus $h\nu$), as shown in the inset of Fig. 1(a). The field effective mobilities of these three TFTs are extracted from the linear region. All of the TFTs show high on-off ratios ($>10^9$). The extracted threshold voltages (V_{th}) for ZnO, $Mg_{0.06}Zn_{0.94}O$, and $Mg_{0.1}Zn_{0.9}O$ TFTs are 2.1 V, 3.5 V, and 4.5 V, respectively. For the ZnO TFT, a field effect mobility μ_{FE} of 30 $cm^2/V\,s$ and a subthreshold swing S of 0.54 V/dec are obtained. Severe degradation of mobility (μ_{FE}=8 $cm^2/V\,s$) and subthreshold swing (S=1.9 V/dec) is observed for the $Mg_{0.1}Zn_{0.9}O$ TFT, resulted from alloying disorder and an increased effective mass of the electrons.[9] However, in contrast to the high Mg composition (10%) case, the $Mg_{0.06}Zn_{0.94}O$ TFT shows the highest field effect mobility (μ_{FE}=40 $cm^2/V\,s$) and lowest subthreshold swing (S=0.25 V/dec). Figure 1(c) shows the hard saturation behavior in the I_{DS}-V_{DS} curve. The maximum bulk trap density (N_{BS}) in the channel can be extracted from the subthreshold swing value, S:[13] $S=(kT/q)\times\log_e 10\times[1+qtN_{BS}/C_{ins}]$, where k is the Boltzmann constant, T is the temperature, q is the elementary charge, t is the thickness of the channel, and C_{ins} is the capacitance of insulator. The extracted values of N_{BS} for ZnO and $Mg_{0.06}Zn_{0.94}O$ TFTs are 3.53×10^{17} cm^{-3} and 1.37×10^{17} cm^{-3}, respectively. The decrease in bulk trap density indicates that the electron traps associated with oxygen vacancies in the ZnO channel are reduced[13] after alloying of 6% Mg to form $Mg_{0.06}Zn_{0.94}O$.

Figures 2(a) and 2(b) show O_{1s} peaks in x-ray photoelectron spectroscopy (XPS) spectra of ZnO and $Mg_{0.06}Zn_{0.94}O$ thin films, respectively. Gaussian fitting is used in the deconvolution of these O_{1s} peaks. The peak at the lower binding energy ~530 eV (O_I) is attributed to O^{2-} ions present in a stoichiometric wurtzite ZnO structure, whereas the peak at the higher binding energy ~532 eV (O_{II}) has been attributed to O^{2-} ions in "oxygen deficient" ZnO.[14] The ratio of peak area (O_{II}/O_{tot}), indicating the relative quantity of this oxygen-related defect, is reduced from 19.3% (for ZnO) to 15.6% (for $Mg_{0.06}Zn_{0.94}O$) after 6% Mg is alloying into the ZnO thin film. Also, the O_I/O_{II} peak positions shifted to lower binding energies from 530.32/532.08 to 530.08/531.80 eV due to a decrease in the number of oxygen vacancies.

Figures 3(a) and 3(b) illustrate the evolution of the transfer characteristics of ZnO and $Mg_{0.06}Zn_{0.94}O$ TFTs at different temperatures, ranging from 300 to 375 K. Both TFTs exhibit a negatively shifted threshold voltage V_{th} with increasing temperature: ΔV_{th} of ZnO TFT and $Mg_{0.06}Zn_{0.94}O$ TFT are 1.5 V and 0.5 V, respectively. The subthreshold drain current of ZnO TFT increases from 2.2×10^{-10} to 8.6×10^{-8} A with a V_{GS} of −2 V. In contrast to the ZnO TFT, the subthreshold drain current of $Mg_{0.06}Zn_{0.94}O$ TFT only increases from 2.3×10^{-10} to 8.0×10^{-9} A with a V_{GS} of 1.5 V. Under a negative gate voltage, neutral oxygen vacancies (V_o) in the depletion region of ZnO channel can be thermally excited to ionized state (V_o^{2+}). Ionized oxygen vacancies would release electrons into the conduction band. The higher channel conductivity and lower V_{th} are induced by the formation of ionized oxygen vacancies. The simulation of the depletion width for deep traps at high concentration[15] shows that with a negative gate voltage of 5 V, the entire channel of the ZnO TFT can be fully depleted under the assumption of trap density $N_T=10^{16}-10^{18}$ cm^{-3}.

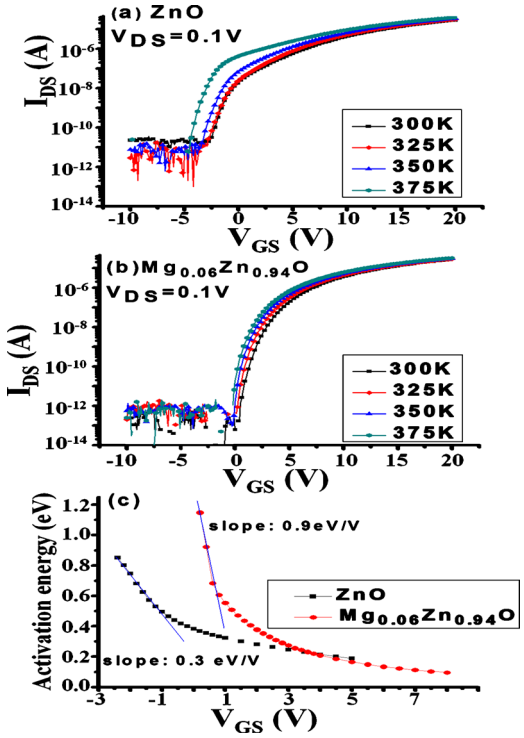

FIG. 3. (Color online) The evolution of transfer characteristics of (a) ZnO TFT and (b) $Mg_{0.06}Zn_{0.94}O$ TFT at different temperatures, ranging from 300 to 375 K. (c) The extracted activation energies as a function of V_{GS} for ZnO and $Mg_{0.06}Zn_{0.94}O$ TFTs.

The activation energy of the drain current extracted from an Arrhenius plot is used to approximately track the position of Fermi level ($E_A=E_C-E_F$) in the band gap. Figure 3(c) shows the activation energy (E_A) of the drain current as a function of V_{GS}. The maximum activation energy of ZnO TFT is 0.85 eV while for $Mg_{0.06}Zn_{0.94}O$ TFT it is 1.15 eV. The increase in activation energy of $Mg_{0.06}Zn_{0.94}O$ TFT cannot be explained only by the increase in the energy band gap since the optical band gap only increases by ~0.15 eV. The higher energy barrier of $Mg_{0.06}Zn_{0.94}O$ TFT may result from the stronger bonding of Mg-O as compared to Zn-O, meaning that the formation of oxygen vacancies is suppressed and the density of oxygen vacancies is also reduced. In addition, the activation energy (E_A) of the $Mg_{0.06}Zn_{0.94}O$ TFT decreases faster as a function of V_{GS}. The falling rate of E_A with respect to V_{GS} is correlated with the filling of traps in the active layer and the gate insulator/active layer interface.[16] For a TFT with a large trap density (N_{tot}), the decrease in E_A with V_{GS} is approximately inversely proportional to the N_{tot}. Because all TFTs are fabricated on the same thermally grown SiO_2/Si film, it can be presumed that most of the contribution of N_{tot} comes from bulk trap density (N_{BS}) of the channel. The faster decrease in E_A (0.9 eV/V) with respect to V_{GS} in the $Mg_{0.06}Zn_{0.94}O$ TFT compared to ZnO TFT (0.3 eV/V) suggests that the N_{tot} in $Mg_{0.06}Zn_{0.94}O$ TFT is diminished by roughly three times relative to a ZnO TFT. This inference is consistent with the value of N_{BS} extracted from the subthreshold slope. Thus, the improved thermal stability and electrical characteristics of $Mg_{0.06}Zn_{0.94}O$ TFT can be mainly attributed to a reduced density of oxygen vacancies and the associated electron traps by incorporation of Mg ions into ZnO.

In summary, with 6% Mg incorporation into a ZnO channel, the field effect mobility and subthreshold swing values are improved. A smaller (negative) shift of threshold voltage and higher activation energy are observed. The improved electrical characteristics and thermal stability of $Mg_{0.06}Zn_{0.94}O$ TFT are mainly attributed to the suppression of oxygen vacancies by introducing stronger Mg-O bonding in the channel layer.

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[1]C. T. Tsai, T. C. Chang, S. C. Chen, I. Lo, S. W. Tsao, M. C. Hung, J. J. Chang, and C. Y. Huang, Appl. Phys. Lett. **96**, 242105 (2010).
[2]A. F. Kohan, G. Ceder, D. Morgan, and C. G. Van de Walle, Phys. Rev. B **61**, 15019 (2000).
[3]K. Vanheusden, C. H. Segar, W. L. Warren, D. R. Tallant, and J. A. Viogt, Appl. Phys. Lett. **68**, 403 (1996).
[4]N. Umezawa, M. Sato, and K. Shiraishi, Appl. Phys. Lett. **93**, 223104 (2008).
[5]Y. Yao and T. Xie, *The Handbook of Physics and Chemistry* (CRC Press, Boca Raton, FL, 1985), Vol. 111.
[6]J. Carrasco, N. Lopez, and F. Illas, Phys. Rev. Lett. **93**, 225502 (2004).
[7]F. K. Shan, B. I. Kim, G. X. Liu, Z. F. Liu, J. Y. Sohn, W. J. Lee, B. C. Shin, and Y. S. Yu, J. Appl. Phys. **95**, 4772 (2004).
[8]A. K. Sharma, J. Narayan, J. F. Muth, C. W. Teng, C. Jin, A. Kvit, R. M. Kolbas, and O. W. Holland, Appl. Phys. Lett. **75**, 3327 (1999).
[9]A. Ohtomo, S. Takagi, K. Tamura, T. Makino, Y. Segawa, H. Koinuma, and M. Kawasaki, Jpn. J. Appl. Phys., Part 2 **45**, L694 (2006).
[10]K. Matsubara, H. Tampo, H. Shibata, A. Yamada, P. Fons, K. Iwata, and S. Niki, Appl. Phys. Lett. **85**, 1374 (2004).
[11]G. H. Kim, W. H. Jeong, B. D. Ahn, H. S. Shin, H. J. Kim, H. J. Kim, M. K. Ryu, K. B. Park, J. B. Seon, and S. Y. Lee, Appl. Phys. Lett. **96**, 163506 (2010).
[12]A. Olziersky, P. Barquinha, A. Vila, L. Pereira, G. Goncalves, E. Fortunato, R. Matins, and J. R. Morante, J. Appl. Phys. **108**, 064505 (2010).
[13]K. Nomura, T. Kayami, H. Ohta, M. Hirano, and H. Hosono, Appl. Phys. Lett. **93**, 192107 (2008).
[14]Y. S. Rim, D. L. Kim, W. H. Jeong, and H. J. Kim, Appl. Phys. Lett. **97**, 233502 (2010).
[15]D. C. Look and J. R. Sizelove, J. Appl. Phys. **78**, 2848 (1995).
[16]K. Takechi, M. Nakata, T. Eguchi, H. Yamaguchi, and S. Kaneko, Jpn. J. Appl. Phys., Part 1 **48**, 011301 (2009).