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High performance thin film transistor with low temperature atomic layer deposition nitrogen-doped ZnO

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High performance thin film transistor (TFT) with atomic layer deposition (ALD) nitrogen doped ZnO (ZnO:N) as an active layer is demonstrated. The electrical properties of ZnO thin films were effectively controlled by *in situ* nitrogen doping using NH_4OH as a source for reactants. Especially, the electron concentration in ZnO was lowered to below 10^{15} cm^{-3}. Good device characteristics were obtained from the inverted staggered type TFTs with ZnO:N channel and ALD Al_2O_3 gate insulator; $\mu_{sat}=6.7$ cm^2/V s, $I_{off}=2.03\times10^{-12}$ A, $I_{on/off}=9.46\times10^7$, and subthreshold swing $=0.67$ V/decade. The entire TFT fabrication processes were carried out at below 150 °C, which is a favorable process for plastic based flexible display. © *2007 American Institute of Physics*.
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The interests for future displays have been significantly increased to create electronic markets, including a flexible and transparent display.[1] However, *a*-Si:H TFT has several limitations for future display applications such as low mobility (below 1.0 cm^2/V s) (Refs. 1) and high photosensitivity.[2] Although poly-Si TFT can solve these problems, the fabrication process requires high process temperature (>250 °C) so Si based TFT cannot be used for transparent display.[1] Recently, transparent oxide semiconductors have been proposed for the active channel layer of TFTs instead of silicon, especially for transparent display.[1,3] Zinc oxide (ZnO) is considered as an attractive candidate since it can be deposited even at room temperature with good electrical and optical properties.[4]

For practical applications of ZnO TFTs, the off current (I_{off}) has to be low enough (<10^{-11} A) since the high I_{off} results in poor on/off ratio leading to problems in switching modulation. Moreover, the carrier mobility has to be large enough to provide stable operation of large-area displays at required video rate.[5] Usually, the ZnO active layers for TFTs have been deposited by physical vapor deposition (PVD) such as direct current (dc) or radio frequency sputtering and pulsed laser deposition.[3,6] Although TFTs with reasonable electrical properties have been reported, the lowest reported value of I_{off} for room temperature PVD ZnO TFT devices has been usually higher than 10^{-10} A. Besides, with upsizing of the display, the PVD may suffer from nonuniformity for large area. For example, the resistivity of PVD ZnO has been reported to be very sensitive to partial oxygen pressure during the deposition.[6] Atomic layer deposition (ALD) produces films of high quality at a relatively low temperature, which makes it very attractive for the fabrication of the TFT on large area flexible substrate. Besides, another potential benefit of ALD process for the fabrication of the TFT is that all the essential components of transparent TFT, including gate, gate insulator, active channel, and source/drain layers, can be deposited by ALD. So far, just a few results have been reported on ALD ZnO TFT.[7] Moreover, improvements in electrical properties are required since the ALD ZnO film has generally unsuitable electrical properties such as high electron carrier concentration (>$10^{18}/cm^3$) and high conductivity.[8]

In this study, we demonstrate the fabrication of high performance TFT devices using an ALD nitrogen doped ZnO film (ZnO:N) as an active channel layer. The nitrogen doping was carried out *in situ* using ammonium hydroxide (NH_4OH) as a source for reactants of ALD ZnO:N. By *in situ* nitrogen doping, the carrier concentration was controlled to proper level for active channel layer of the TFT devices. By employing ALD Al_2O_3 at a low growth temperature ($T_s=150$ °C) as a gate insulator, high performance ZnO TFT devices were fabricated with high saturation mobility (6.7 cm^2/V s), low I_{off} (2.0×10^{-12} A), high $I_{on/off}$ (9.5×10^7), and very low hysteresis (<0.5 V).

The undoped and nitrogen doped ZnO thin films were deposited on both glass (Corning 1737) and silicon (001) substrates by ALD with diethyl zinc (DEZ) as a precursor. For nitrogen doped ZnO, diluted NH_4OH solution was employed as a single source for reactants. The ALD has been carried out at various growth temperatures between 100 and 200 °C. The film thicknesses were measured routinely by ellipsometer (Rudolph auto ELII). The chemical compositions and bonding states were determined by x-ray photoelectron spectroscopy (XPS) (Escalab 220 iX). The microstructure of ALD ZnO was analyzed by x-ray diffraction (Rigaku Rint2500) and the surface roughness and lateral grain diameter were obtained from DI NanoScope IIIa Multimode atomic force microscopy (AFM). The optical transmittance measurements of the glass substrate, ZnO/Al_2O_3/glass, and $ZnO:N/Al_2O_3$/glass samples were carried out by a Shimadzu UV1700 UV-Vis spectrometer in the wavelength range from 200 to 1100 nm. The resistivity and Hall mobility of ZnO thin films were measured by Hall measurement system (Accent Optical Technologies HL5500PC). TFTs, which were staggered inverted type, with

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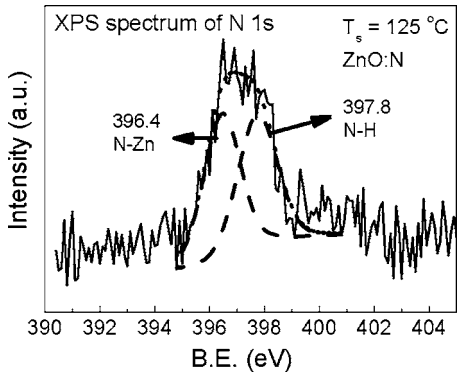

FIG. 1. XPS spectrum in N 1*s* binding energy region of ALD ZnO:N at T_s=125 °C.

various channel widths (W) and channel lengths (L) were produced by conventional photolithography. As a first step of TFT fabrication, 100 nm thick Ti, prepared by dc magnetron sputtering at room temperature, was patterned by photolithography and wet etching to form gate electrode. Subsequently, 97 nm thick ALD Al_2O_3 thin films was deposited as a gate insulator at T_s=150 °C by using tri-methyl-aluminum and H_2O. The dielectric constant of the deposited Al_2O_3 films was 8.5, which was obtained from separate *C-V* measurements. ALD ZnO or ZnO:N film as an active channel layer was also patterned by photolithography and wet etching. Finally, 100 nm thick Ti source/drain (S/D) layers were patterned by lift-off technique. Device characteristics, including transfer and output curves, were measured by semiconductor parameter analyzer (Keithley 4200) with three probes.

The growth rate of ALD ZnO at saturation conditions was 1.6 Å/cycle, as reported previously.[8] The growth rate was not affected by nitrogen doping. This good saturation in growth rates suggests that the ALD growth mode was achieved. The x-ray diffraction spectrum of undoped ALD ZnO film shows a predominant (002) diffraction peak with small (100) and (101) diffraction peaks, indicating the (002) preferred orientation. For ALD ZnO:N, however, the (002) peak intensity is reduced significantly, while the (100) and (101) peak intensities remain almost the same. (Data not shown) In addition, AFM measurements have shown that although the root mean square roughnesses of ALD ZnO and ZnO:N films are almost the same (2.3 versus 2.8 nm, respectively), the average grain diameter of ZnO is 66±14.1 nm and that of ZnO:N is 51±6.4 nm. Thus, nitrogen doping produces smaller grain size with more uniform grain size distribution.

Figure 1 shows the XPS spectrum of ALD ZnO:N film in the N 1*s* binding energy region, deposited on ALD Al_2O_3/Si substrate at T_s=125 °C. The broad peak at around 397 eV is deconvoluted to two peaks; one peak at 396.4 eV from N–Zn bond and the other peak at 397.8 eV from N–H bond. Thus, we infer that nitrogen atoms are incorporated as Zn–NH_x, which agrees with previous reports on nitrogen doped CVD ZnO.[9] Especially for our low temperature ALD process, most of nitrogen atoms are thought to be incorporated as NH_x, since the thermal energy is not high enough to break all N–H bonds of NH_3 molecules. From the peak intensity, the nitrogen concentration in ALD ZnO:N film was estimated to be around 3.5 at. %. Besides the nitrogen, no other impurity such as carbon was detected.

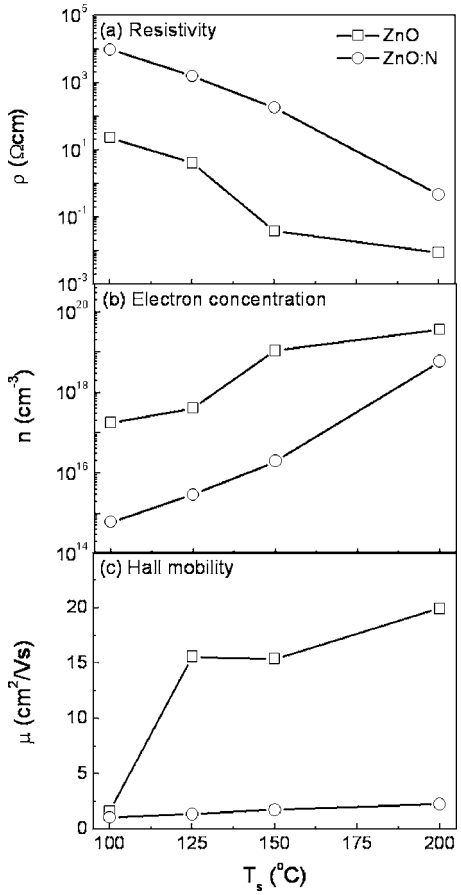

FIG. 2. Electrical properties of ALD ZnO and ZnO:N thin films prepared at T_s=100–200 °C (a) resistivity, (b) carrier concentration, and (c) Hall mobility.

The electrical properties of ALD ZnO film were significantly changed by nitrogen doping. Figure 2 shows the resistivity, Hall mobility, and carrier concentrations of ALD ZnO and ZnO:N as a function of growth temperatures. For all the growth temperatures, the resistivity values increase almost by three orders of magnitude by nitrogen doping [Fig. 2(a)]. This large increase in resistivity is due to the significant decrease in carrier concentration, as shown in Fig. 2(b). Undoped ALD ZnO films show intrinsically *n*-type carrier conductivity with high carrier concentration up to 5×10^{19} cm^{-3}. However, we obtained very low carrier concentration down to 6×10^{14} cm^{-3} by nitrogen doping, especially at a low growth temperature. The mobility of ALD ZnO was reduced by nitrogen doping [Fig. 2(c)], probably due to the impurity scattering.[10] Our XPS results indicate that most of nitrogen atoms are incorporated as NH_x due to the use of NH_3 for N source and the low growth temperature. For this molecular configuration, the nitrogen is electrically passivated by H.[10] Due to this, we infer that although over 3.5 at. % nitrogen has been incorporated, most of nitrogen atoms are electrically neutral and only a small portion of nitrogen atoms are consumed to compensate the *n*-type carriers. In addition, the transmittance measurements show that the transmittance of the ALD ZnO (80 nm thick)/Al_2O_3/glass sample is over 80% in the range of visible wave length (400–800 nm). Similarly, ALD ZnO:N (66 nm thick)/Al_2O_3/glass sample also shows high transmittance over 80% in the most of the range of visible wave length.

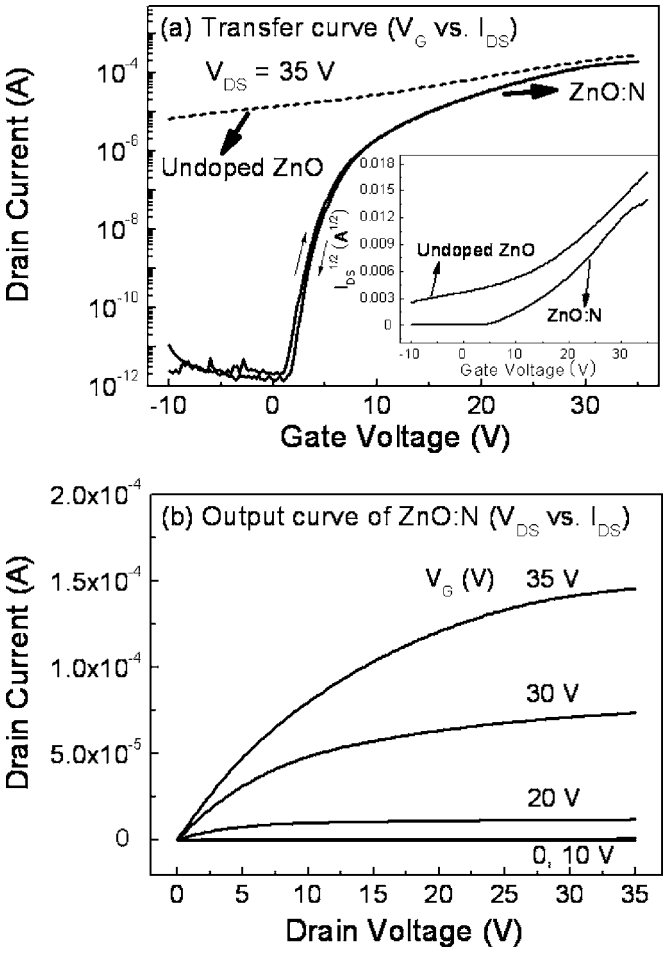

FIG. 3. (a) Transfer curves of TFTs with ZnO and ZnO:N active layer, respectively. (The inset represents V_G vs root of I_{DS} curve). (b) Output curves on ZnO:N TFT.

Inverted staggered type TFTs (with bottom gate and top contact) with various channel widths (20–40 μm) and channel lengths (20–100 μm) were fabricated using ALD ZnO and ZnO:N deposited at T_s=125 °C as active layers and ALD Al_2O_3 deposited at T_s=150 °C as a gate insulator. It should be noticed that all the device fabrication processes were carried out at below 150 °C, as described in the experimental session. Figure 3(a) shows the transfer curves [gate voltage (V_G) versus drain current (I_{DS})] for the TFTs using ALD ZnO and ZnO:N as active layers. The width, length, and source/drain and gate overlap of these TFT devices are 40, 20, and 5 μm, respectively. The thicknesses of ALD ZnO and ZnO:N are 80 and 66 nm, respectively, and the thickness of the ALD Al_2O_3 gate insulator is 97 nm for both cases. The transfer curves were measured under 35 V of drain voltage (V_{DS}). As shown in Fig. 3(a), the TFT made with undoped ZnO as a channel does not show proper transistor characteristics. The general pinch-off and depletion phenomena were not observed during V_G sweeping. This behavior is expected when we consider that the undoped ALD ZnO has unacceptably high carrier concentration over $10^{17}/cm^3$. On the contrary, ALD ZnO:N TFT shows typical behaviors of the *n*-channel enhancement mode TFT device. The output curves (V_{DS} versus I_{DS}) of ZnO:N TFT measured at V_{DS}=0–35 V under various V_G (0–35 V) are shown in Fig. 3(b). The output curves exhibit clear pinch-off and current saturation, indicating that the operation of this TFT device conforms to the standard field-effect transistor theory and the Fermi level in the channel is fully controlled by the gate and drain bias.

The threshold voltage (V_{th}) and the saturation mobility (μ_{sat}) were obtained by fitting the straight line of the square root of I_{DS} versus V_G [shown as an inset in Fig. 3(a)]. The μ_{sat} was about 6.7 cm^2/V s and V_{th} was 4.1 V, showing that the ZnO:N TFT operated in the enhancement mode, leading to the decrease in the power consumption. For the various channel widths and lengths, no significant difference in device performances was observed. Also, a short channel effect was not observed for the channel lengths down to 20 μm. More importantly, excellent off-current (I_{off}) (2.03×10^{-12} A) and on/off ratio ($I_{on/off}$) (9.46×10^7) were obtained for the ALD ZnO:N TFTs, which are comparable to *a*-Si:H or poly-Si TFT. Although higher mobility values were obtained for PVD based ZnO TFTs in several previous reports,[1,3,6,11] they have limitations in the practical applications due to high I_{off} current ($>10^{-10}$ A). Moreover, the hysteresis of ALD ZnO:N TFT was <0.5 V, indicating that the gate insulator and active layer have very small charge traps ($D_t \sim C_i \Delta V_G/q = 2.49\times10^{11}/cm^2$). In addition, the subthreshold swing of the device was 0.67 V/decade, which is relatively small, compared to other previous reports.[3,6]

All these results indicate that the nitrogen doping to ALD ZnO drastically improves the electrical properties as an active channel layer of TFT devices and is expected to be a valuable technique for the fabrication of the practical and stable TFT devices. Due to the many great benefits of ALD including a low growth temperature and large area uniformity, ALD based thin films should be considered as a promising candidate for the next generation display device fabrication. Additionally, we expect that nitrogen-doping technique during ALD process proposed in the current study would find various applications in many other materials system.

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