

Optical and electrical properties of N-doped ZnO and fabrication of thin-film transistors*

Zhu Xiaming(朱夏明)¹, Wu Huizhen(吴惠桢)^{1,2,†}, Wang Shuangjiang(王双江)¹, Zhang Yingying(张莹莹)¹,
Cai Chunfeng(蔡春锋)¹, Si Jianxiao(斯剑霄)¹, Yuan Zijian(原子健)¹,
Du Xiaoyang(杜晓阳)³, and Dong Shurong(董树荣)³

(1 Department of Physics, Zhejiang University, Hangzhou 310027, China)

(2 State Key Laboratory of Modern Optical Instrumentations, Zhejiang University, Hangzhou 310027, China)

(3 ESD Laboratory, Institute of Microelectronics and Photoelectronics, Zhejiang University, Hang Zhou 310027, China)

Abstract: Using NH_3 as nitrogen source gas, N-doped ZnO (ZnO:N) thin films in *c*-axis orientation were deposited on glass substrates by radio frequency magnetron sputtering at room temperature. The ZnO:N thin films display significant increase of resistivity and decrease of photoluminescence intensity. As-grown ZnO:N material was used as active channel layer and Si_3N_4 was used as gate insulator to fabricate thin-film transistor. The fabricated devices on glasses demonstrate typical field effect transistor characteristics.

Key words: ZnO; N-doping; resistivity; photoluminescence; thin film transistors

DOI: 10.1088/1674-4926/30/3/033001

PACC: 7280E

1. Introduction

With the development of growth of thin films and micro-manufacturing technology, thin film transistors (TFTs) have been widely used in many fields. The properties of TFT channel layers that are semiconductor materials play a vital role in the devices and determine the application fields of the devices. In recent years, considerable attention has been paid to transparent TFTs using ZnO as channel layers^[1-6]. ZnO is a II-VI wide-band gap (3.37 eV at RT) semiconductor material. It has a large exciton binding energy (60 meV) and it is also highly transparent in visible light region. Furthermore, ZnO thin films with highly *c*-axis preferred orientation^[7] can be deposited on a variety of substrates at relative low temperature. Because of these properties, TFTs using ZnO as channel layers display better characteristics than that with traditional channel materials such as amorphous silicon, polycrystalline silicon and organic semiconductors. Therefore ZnO transparent TFTs could be the promising electronic devices to realize the next generation of active-matrix liquid-crystal display (AMLCD)^[1-4].

Magnetron sputtering has several advantages over other deposition methods such as evaporation or chemical vapor deposition^[8]: (a) low deposition temperature (or RT); (b) good cohesiveness to substrates; (c) uniform thickness and good densification; (d) batch production in wide area and a relatively cheap growth method. Recently, magnetron sputtering has been used widely in industry, such as integrated circuit (metal thin films), transparent and conductive thin films for flat panel display (transparent conductive oxide thin films) and building glasses (low radiation films). In 2003, Hoffman *et al.*^[1] deposited ZnO thin films as channel layers of TFTs on

transparent $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) coated glasses by ion beam sputtering and realized high transparent ZnO-TFT devices. Wu *et al.*^[5,6] developed enhancement mode ZnO-TFT devices with a wide-gap hexagonal phase crystal ZnMgO semiconductor as channel layers and cubic phase crystal ZnMgO as gate insulation layers.

There are defects in undoped ZnO such as oxygen vacancies (V_O) and Zn interstitials (Zn_i) which act as donors and provide free electrons. As a result, ZnO thin films often show high carrier concentration. These defects also increase the scattering probability when carriers transport in the crystal and decrease the carrier mobility. In the fabrication of ZnO-TFT devices, it is a key issue to decrease the density of defects in channel layers and lower carrier concentration by which good gate control of carrier distribution in channel layers and high carrier mobility could be realized. Wu *et al.*^[6] realized ZnMgO ternary alloys by doping Mg in ZnO which leads to the increase of band gap and decrease of electron concentration. Zhang *et al.*^[9] realized reduction of electron concentration by the introduction of acceptor energy levels by doping N in ZnO. However, they fabricated ZnO-TFT on thermally oxidized p-Si as substrates by laser molecular beam epitaxy (L-MBE) which may increase production cost.

N has been considered as a possible good candidate for realizing p-ZnO because the radius of N atoms are close to O atoms and N atoms can substitute O lattice positions by the formation of acceptors. N^{3-} occupying a lattice position of O^{2-} forms an acceptor by doping N in the deposition of ZnO, which can compensate O vacancies and decrease the density of defects and the concentration of conduction electrons. In this paper, we fabricate ZnO:N thin films on glasses with high *c*-axis orientation by RF magnetron sputtering using Ar as

* Project supported by the National Natural Science Foundation of China (No. 60676003) and the Natural Science Foundation of Zhejiang Province (No. Z406092).

† Corresponding author. Email: hzwwu@zju.edu.cn

Received 27 June 2008, revised manuscript received 29 September 2008

© 2009 Chinese Institute of Electronics

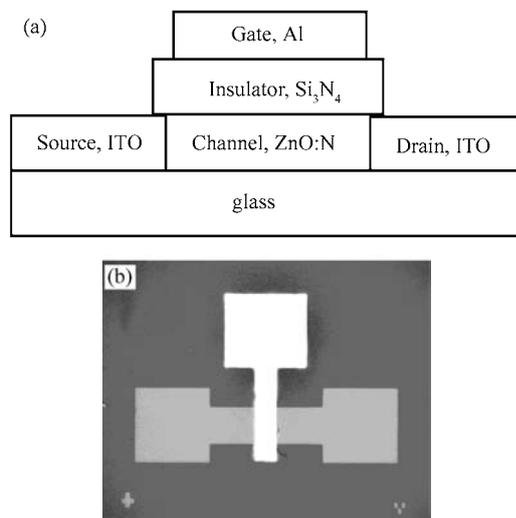


Fig. 1. (a) Schematic cross-sectional view; (b) Photo of a top-gate ZnO TFT.

sputtering gas and NH_3 as doping gas. We find that the resistivity of ZnO increased significantly and the intensity of PL decreased in the ZnO:N. The n-type ZnO-TFTs deposited at RT using ZnO:N as channel layers show that gate voltage modulates the electron concentration in the channel layers.

2. Experiment

2.1. ZnO thin films

We deposited ZnO thin films on glasses by RF magnetron sputtering using high purity ZnO (99.99%) as a sputtering target, high purity Ar (99.999%) as sputtering gas and high purity NH_3 (99.999%) as doping gas. The base pressure of the growth chamber was below 6.6×10^{-4} Pa. A flow rate of Ar gas was 6 sccm. We have grown a series of samples by changing the flow rates of NH_3 with the same sputtering power (180 W) and substrate temperature (400 °C). X-ray diffraction (XRD) showed that the ZnO thin films with these growth parameters have obviously polycrystalline structures. In addition, we obtained the ZnO:N thin films with high *c*-axis orientation by lowering sputtering power to 100 W and keeping substrates at RT, because low sputtering power can lighten the damage to growth surface and decrease the stress in thin films which is caused by the bombardment of high-energy radio frequency ionized anions.

2.2. ZnO-TFT devices

We used ITO-coated glasses as conductive substrates and adopted top gate structure. The cross sectional view is shown in Fig. 1(a). Source and drain electrodes are patterned on ITO by standard photolithography and wet etching. Then ZnO:N was deposited as channel layers by magnetron sputtering. The growth parameters were as follows: RT, a sputtering power of 100 W, and the flow rates of Ar and NH_3 gases being 6 and 1 sccm, respectively.

The width and length of the channel layers were 100 and 20 μm respectively, and the thickness of channel was 80 nm. Then a Si_3N_4 layer with a thickness of 120 nm was deposited

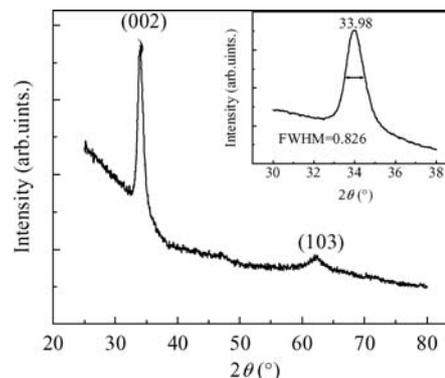


Fig. 2. XRD pattern of the ZnO:N thin film.

by plasma enhanced chemical vapor deposition (PECVD). A thin film with the thickness of about 500 nm was deposited as gate electrode by thermal evaporation. Figure 1(b) shows the photo of a TFT device taken from an optical microscope.

2.3. Properties measurements

The lattice structure of ZnO thin films was measured by X-ray diffraction (XRD) with a PANalytical X'Pert PRO system. Photoluminescence (PL) spectra were measured by Edinburgh Instruments FLS-920 photoluminescence spectrograph at RT. A He-Cd laser with a laser line of 325 nm was used as excitation source. Capacity-voltage (*C-V*) characteristics of ZnO-TFTs were measured by an HP 4280 impedance analyzer at high frequency (1 MHz). $I_{\text{DS}}-V_{\text{DS}}$ was measured by a Keithley 4200-SCS semiconductor characterization system.

3. Results and discussion

XRD measurement results of ZnO deposited on glasses at RT with a sputtering power of 100 W and the NH_3 flow rate of 1 sccm are shown in Fig. 2. It can be seen that the ZnO:N thin films were hexagonal wurtzite structure with *c*-axis orientation perpendicular to the substrate surface. The XRD peak of (002) crystal planes is at $2\theta = 33.98^\circ$ which is 0.43° smaller than bulk ZnO crystal (34.41°). This may result from the strain in the film because the sample was not annealed. The FWHM of (002) peak is 0.826° . We could estimate the average size of the ZnO:N crystalline grain by Scherrer formula (1)^[10]:

$$t = \frac{0.9\lambda}{B \cos \theta}, \quad (1)$$

where *t* is the grain size, λ is the wavelength of X-ray (0.154 nm), *B* is the FWHM, and θ is the half diffraction angle of crystal orientation peak. The grain size calculated is about 10 nm which means that the film is composed of nanocrystallites. In Fig. 2 there is also a smaller peak at $2\theta = 62.38^\circ$ which corresponds to the diffraction of (103) crystal planes. This result shows that the films grown at low temperature generally display polycrystalline structure.

We also measured photoluminescence (PL) spectra of the ZnO:N samples. Because glass substrates also have a PL peak near 380 nm that is close to the peak of ZnO, in order to avoid mis-interpretation of the origin of PL, two samples were grown on Si substrates for PL measurements. The growth parameters were: a sputtering power of 100 W, the Ar flow rate

Table 1. Growth parameters and resistivities of the ZnO:N thin films.

Sample	Growth temp. (°C)	RF power (W)	Ar flow rate (sccm)	NH ₃ flow rate (sccm)	Film thickness (nm)	Resistivity (Ω·cm)
C	400	180	26	0	110	1.21×10^3
D	400	180	6	0.75	515	1.78×10^5
E	400	180	6	1.0	470	1.68×10^5
F	400	180	6	1.5	475	2.30×10^4
G	400	180	6	3.0	270	2.36×10^3
H	400	180	6	6.0	295	2.58×10^3
I	400	180	6	7.5	315	1.09×10^5

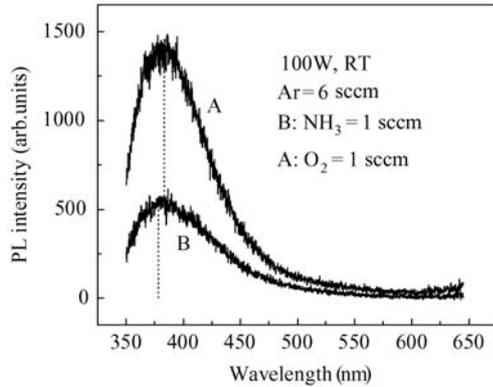


Fig. 3. PL spectra of the ZnO thin films on Si substrates at RT.

of 6 sccm, RT and the same growth time of 60 min for the two samples. Sample A is used for comparison which was grown with 1 sccm O₂ flow rate. Sample B was doped with N and the flow rate of NH₃ was 1 sccm. PL at RT is shown in Fig. 3. Two samples show PL peaks in near ultra-violet region: the peak of sample A is at 383 nm (3.25 eV) and the peak of sample B is at 378 nm (3.27 eV). It can be seen that the PL peak of B blue shifts 5 nm and its intensity is only one of third of sample A and its FWHM becomes large as well.

The PL peaks in the above samples are similar to ZnO bulk material, which shows that the PL emission originates from the recombination of free excitons. In the process of radiative recombination of direct band gap semiconductor materials, radiative recombination rates depend on carrier density of upper energy states n_u , vacant density of lower energy states n_l' and the transition probability from the upper electronic states to the lower vacant states $W_{ul}^{em[11]}$. That is

$$R(\hbar\omega) \propto n_u n_l' W_{ul}^{em}. \quad (2)$$

For n-type semiconductor materials, $n_0 \gg p_0$, we have $\Delta n \ll n_0$, $\Delta p \ll n_0$, $\Delta p \gg p_0$ in a small carrier injection by external light illumination conditions, where n_0 is the majority carrier concentration, p_0 is the minority carrier concentration at an equilibrium condition, and Δn is the non-equilibrium majority carrier concentration, Δp is the non-equilibrium minority carrier concentration.

From $n_u = n_0 + \Delta n \approx n_0$, $n_l' = (p_0 + \Delta p) \approx \Delta p$, Equation (2) can be expressed as

$$R(\hbar\omega) \propto n_0 \Delta p W_{ul}^{em}. \quad (2')$$

In ZnO:N, N atoms could substitute O by the formation

of acceptors, which would decrease density of free electrons in ZnO thin films. We measured conductivity of ZnO:N thin films by Seebeck effect and found it is still n-type though N is doped in ZnO. From the measured electrical resistivity results, we can obtain that n_0 significantly decreased after N-doping in ZnO. We assumed that W_{ul}^{em} is independent of N doping in ZnO, Δp excited by pumping laser keeps nearly unchanged. We can know from Eq. (2') that the radiative recombination rate R for ZnO:N thin films significantly decreases. In our PL measurement, the sampling time of the detector was fixed. Therefore, the PL intensity of B was much smaller than that of sample A.

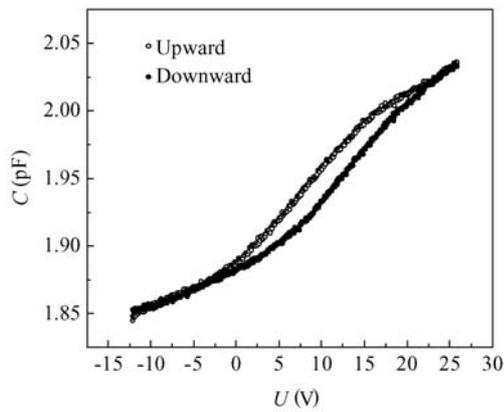
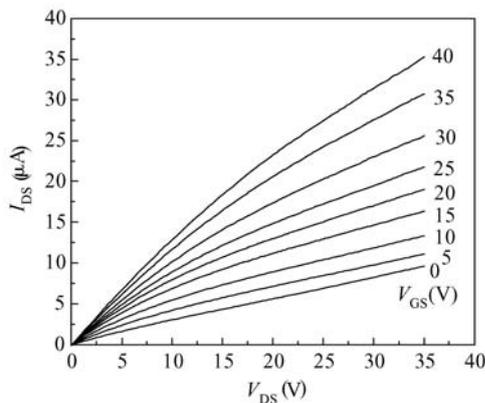
We also measured the resistivity of ZnO:N thin films which were grown at a same substrate temperature of 400 °C, and same RF power of 180 W, but with different NH₃ flow rates. The results are listed in Table 1. Sample C is used for comparison which was deposited without NH₃ and the flow rate of Ar was 26 sccm. We can see that the resistivity of ZnO:N significantly increased after doping of N, which indicates that N atoms substitute O by the formation of acceptors and reduce electron concentration in ZnO:N thin films. But the resistivity decreases with the increase of the NH₃ flow rate and reaches to minimum when the flow rate is 3 sccm. And the resistivity of the ZnO:N thin films increases again with further increase of the NH₃ flow rates.

NH₃ will be ionized into nitrogen ions and hydrogen ions by RF power action:



The densities of nitrogen ions and hydrogen ions in the growth chamber increase with the rise of the NH₃ flow rates. It can be seen from Eq. (3) the density of hydrogen ions increases faster than that of N. Therefore the possibility of H ions entering into the ZnO thin films and forming donors also rises faster. The formation of donors would compensate the formation of N acceptors in ZnO:N. The resistivity increases again when NH₃ flow rate further increase from 3 sccm. This may be due to the possible saturation of hydrogen entering into ZnO thin films, but the details of the internal mechanism were not clear. As a conclusion, the doping of NH₃ increases the resistivity of ZnO thin films by reducing electron concentration. In the fabrication of ZnO-TFTs, we chose a lower NH₃ flow rate (1 sccm) for ZnO channel material growth.

Figure 4 shows the capacitance–voltage (C – V) charac-

Fig. 4. C - V characteristics of a ZnO:N TFT.Fig. 5. I_{DS} - V_{DS} characteristics of a ZnO:N TFT.

teristic curve measured at a high frequency of 1 MHz for the ZnO-TFT devices which consist of Al electrode, Si_3N_4 insulator and ZnO:N channel. The capacitance slowly increases with the rise of bias voltage until saturation, indicating a typical n-type semiconductor of the ZnO:N channel.

Figure 5 shows the I_{DS} - V_{DS} curves measured at RT for a ZnO:N TFT. We can see that gate voltage V_{GS} modulates the output characteristics (I_{DS} - V_{DS}) of the ZnO:N TFT. The drain current I_{DS} significantly increases as V_{GS} increases. This also shows that the channel layer of the fabricated ZnO:N TFT device is an n-type semiconductor, being consistent with the above C - V result. For a fixed V_{GS} , I_{DS} rises with the increase of applied drain voltage V_{DS} and shows a saturation trend. But I_{DS} is relatively large and increases almost linearly with the rise of V_{DS} when $V_{GS} = 0$ V. For example, when $V_{DS} = 35$ V, the drain current is $I_{DS} = 9.6 \mu\text{A}$. This means that electron concentration in the channel layer could be high. For ZnO:N thin films grown in a NH_3 ambience, H ions could tunnel into ZnO lattice and occupy interstitial positions close to N while N atoms substitute O lattices which may lead to the formation of N_O -H complexes in ZnO thin films. N_O -H complexes donate electrons and compensate density of N acceptors in ZnO. However, annealing would break off the N_O -H chemi-

cal bonds and make doped N as effective acceptors^[9].

We also measured the leakage current I_{GS} which was nano-ampere in magnitude, much smaller than I_{DS} . Gate leakage current having no impact on output characteristic of the TFT device indicates Si_3N_4 has good insulating properties in this device.

4. Conclusion

We fabricated ZnO:N thin films on glass substrates by RF sputtering using NH_3 as doping gas. The ZnO:N crystal shows c -axis preferred orientation. PL measurements show that the PL peak intensity of ZnO thin films decreases after N-doping. The electrical measurement results show that the resistivity of ZnO thin films is significantly increased after N-doping. We also used these ZnO:N thin films as channel layers and fabricated TFT devices. These TFT devices show gate voltage control and modulation to source-drain current in ZnO channel layers.

References

- [1] Hoffman R L, Norris B J, Wager J F. ZnO-based transparent thin-film transistors. *Appl Phys Lett*, 2003, 82(5): 733
- [2] Garcia P F, McLean R S, Reilly M H, et al. Transparent ZnO thin-film transistor fabricated by rf magnetron sputtering. *Appl Phys Lett*, 2003, 82(7):1117
- [3] Fortunato E M C, Barquinha P M C, Acmbg P, et al. Fully transparent ZnO thin-film transistor produced at room temperature. *Adv Mater*, 2005, 17(5): 590
- [4] Liu C C, Chen Y S, Huang J J. High-performance ZnO thin-film transistors fabricated at low temperature on glass substrates. *Electron Lett*, 2006, 42(14): 824
- [5] Wu Huizhen, Liang Jun, Lao Yanfeng, et al. Electrical properties of wide bandgap ZnMgO and fabrication of transparent thin film transistors. *Chinese Journal of Semiconductors*, 2006, 27(Suppl): 218 (in Chinese)
- [6] Wu H Z, Liang J, Jin G F, et al. Transparent thin-film transistors using ZnMgO as dielectrics and channel. *IEEE Trans Electron Devices*, 2007, 54(11): 2856
- [7] Wu H Z, He K M, Qiu D J, et al. Low-temperature epitaxy of ZnO films on Si(001) and silica by reactive e-beam evaporation. *J Cryst Growth*, 2000, 217(1/2): 131
- [8] Ellmer K. Magnetron sputtering of transparent conductive zinc oxide: relation between the sputtering parameters and the electronic properties. *J Phys D: Appl Phys*, 2000, 33(4): R17
- [9] Zhang X A, Zhang J W, Zhang W F, et al. Enhancement-mode thin film transistor with nitrogen-doped ZnO channel layer deposited by laser molecular beam epitaxy. *Thin Solid Films*, 2008, 516(10): 3305
- [10] Tu M L, Su Y K, Ma C Y. Nitrogen-doped p-type ZnO films prepared from nitrogen gas radio-frequency magnetron sputtering. *J Appl Phys*, 2006, 100(5): 053705
- [11] Shen Xuechu. Spectroscopic and optical property of semiconductor. Beijing: Science Press, 2002 (in Chinese)