Control and improvement of *p*-type conductivity in indium and nitrogen codoped ZnO thin films

L. L. Chen
State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China and Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

Z. Z. Ye[a),b)] and J. G. Lu
State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

Paul K. Chu[a),c)]
Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

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p-type ZnO thin films have been fabricated by In and N codoping. The carrier type in the In–N codoped ZnO can be controlled by adjusting the growth conditions and good *p*-type conductivity is obtained at temperatures between 490 and 580 °C. The *p*-type behavior is improved when a buffer layer is used. The lowest reliable room temperature resistivity is found to be 7.85 Ω cm in the presence of a buffer layer. The ZnO-based homostructural *p*-*n* junctions comprising a *n*-ZnO:In layer on a *p*-ZnO:(In,N) layer on a buffer layer display apparent electrical rectification in the authors' repeated measurements. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2405858]

ZnO, with a direct band gap of 3.37 eV, has a higher exciton binding energy (60 meV) and optical gain ($320\ cm^{-1}$) than GaN.[1] However, problems associated with *p*-type conductivity have impeded the use of ZnO in light-emitting diodes and laser diodes in the blue, violet, and ultraviolet regions.[2,3] Nitrogen, a good *p*-type dopant in other II-VI semiconductors,[4,5] has long been considered a possible *p*-type dopant in ZnO. Incorporation of both acceptors and reactive donors has been proposed to increase the solubility of N in ZnO.[6] The synthesis of *p*-type ZnO films with acceptable stability and reproducibility by means of indium and nitrogen codoping has recently been demonstrated.[7] For device fabrication, a good understanding of the doping behavior of In and N in *p*-type ZnO is required. Here, we report the control of the carrier type in In–N codoped ZnO films by adjusting the growth conditions and the improvement of *p*-type conductivity by means of a high temperature buffer layer.

ZnO films were synthesized on glass substrates by direct current reactive magnetron sputtering. An In_xZn_{1-x} ($x=0.8$ at. %) alloy (99.999% purity) was used as the codoping target. The deposition chamber was initially evacuated to a base pressure of 10^{-3} Pa and then a mixture of Ar (99.995%) and N_2O (99.99%) with a ratio of 1:1 was introduced as the sputtering gas at a total pressure of 4 Pa. The films were deposited at various substrate temperatures from 400 to 600 °C. Before deposition, the target was presputtered for 10 min to remove surface contaminants. The sputtering time, current, and voltage were 30 min, 200 mA, and 200 V, respectively. The working gas continued to flow into the deposition chamber after the sputtering had stopped until the substrate temperature returned to room temperature. The electrical properties were investigated by Hall-effect measurements using the Van der Pauw system (Bio-Rad HL5500PC) at room temperature. The current-voltage (*I*-*V*) characteristics were determined by an Agilent Technologies 4140B and Signaton Probe Station.

Table I shows the dependence of the electrical properties of the In–N codoped ZnO films on temperature. To examine the reliability of the results, the electrical measurements were carried out three times and similar results were observed. At low temperatures ($400\ °C \leq t \leq 480\ °C$), the films possess rather high resistivity and the carrier type is ambiguous. At intermediate temperatures ($490\ °C \leq t \leq 580\ °C$), *p*-type

TABLE I. Electrical properties of In–N codoped ZnO films produced at different temperatures.

Temperature (°C)	Carrier type	Resistivity (Ω cm)	Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)	Carrier concentration (cm^{-3})
400	⋯	1.70×10^5	1.36	2.70×10^{13}
450	⋯	1.31×10^5	2.73	1.75×10^{13}
460	⋯	7.45×10^4	3.07	2.73×10^{13}
470	⋯	1.37×10^4	2.98	1.53×10^{14}
480	⋯	1.39×10^4	2.15	1.21×10^{14}
490	*p*	4.15×10^3	1.11	1.78×10^{15}
500	*p*	2.32×10^3	0.746	2.52×10^{15}
510	*p*	640	0.245	3.98×10^{16}
520	*p*	120	0.363	1.43×10^{17}
530	*p*	69.4	0.711	1.26×10^{17}
540	*p*	23.7	0.752	3.51×10^{17}
550	*p*	45.8	0.815	1.67×10^{17}
560	*p*	67.9	1.62	5.69×10^{16}
570	*p*	128	1.19	4.09×10^{16}
580	*p*	211	1.58	1.87×10^{16}
590	*n*	2.77×10^3	1.93	1.17×10^{15}
600	*n*	793	0.113	6.94×10^{16}

[a)]Author to whom correspondence should be addressed.
[b)]Electronic mail: yezz@zju.edu.cn
[c)]Electronic mail: paul.chu@cityu.edu.hk

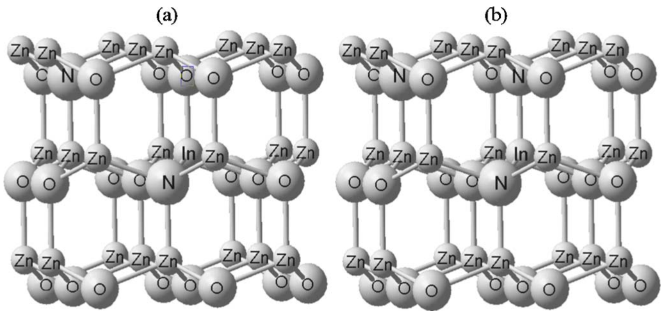

FIG. 1. Schematic of the crystal structures of the supercells in the In–N codoped ZnO thin films produced in the intermediate temperature region. (a) shows the In–2N pair and (b) shows the In–3N pair.

conductivity is achieved. The optimal results, namely, resistivity of 23.7 Ω cm, carrier concentration of 3.51×10^{17} cm^{-3}, and Hall mobility of 0.752 $cm^2\,V^{-1}\,s^{-1}$, are obtained when the substrate temperature is 540 °C. At high temperatures ($t \geqslant 590$ °C), the carrier type changes from *p* to *n*, and *n*-type conductivity is enhanced with increasing temperature. Our results thus show that the carrier type in In–N codoped ZnO films can be controlled by adjusting the growth conditions during film deposition. The results may be understood as follows.

In the low temperature region, there are three possible reasons for the ambiguous carrier type. Firstly, from the thermodynamics point of view, a low temperature is better for nonequilibrium growth and so it bodes well for N doping. However, it also benefits the formation of N_2-on-O substitution $[(N_2)O]$ which is a double shallow donor in ZnO.[8] Thus, self-compensation may result. Secondly, a low temperature commonly leads to poor crystallization, thereby inducing more defects and leading to a low carrier concentration. Thirdly, at a low temperature, H atoms may easily bond to the N atoms as the thermal energy is not sufficient to remove the hydrogen atoms from the film. It is known that H deactivates the N acceptor. Accordingly, ambiguous carrier-type conduction is observed.

In the intermediate temperature regions, the conditions are apparently suitable for forming *p*-type conductivity in ZnO as confirmed by the good results. The appropriate growth temperature provides the necessary conditions as described above. Theoretically, In and N in the codoped ZnO form In-centered complexes. Here, we assume that the main forms are In–2N pair and/or In–3N pair, which is one of the basic requirements for observing *p*-type behavior in codoped ZnO as predicted by theoretical calculation.[9] For the In–2N pair [Fig. 1(a)], the first N atom occupies the nearest neighbor site of In and the second one is located at the next-nearest-neighbor site of In. For the In–3N pair [Fig. 1(b)], the first two N atoms are the nearest neighbors to In and the third one is the next-nearest neighbor to In.

In the high temperature region, one of the main reasons for the *p*-type degradation is the dissociation of In–2N or In–3N complexes. As the complexes dissociate, the nitrogen concentration decreases while the solubility of In is still high, thus forming donors in ZnO. From the viewpoint of thermodynamics, equilibrium growth will occur at high temperature and it is not good for N doping. Accordingly, *n*-type conductivity emerges.

Thermodynamically, a higher temperature is better for crystal growth but an intermediate temperature is necessary

TABLE II. Electrical properties of In–N codoped ZnO films without a buffer layer (sample I) and with a buffer layer (sample II).

Sample	Carrier type	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Hall mobility ($cm^2\,V^{-1}\,s^{-1}$)
I	*p*	23.7	3.51×10^{17}	0.752
II	*p*	7.85	5.40×10^{17}	1.47
II (30 days later)	*p*	7.85	5.84×10^{17}	1.36

to achieve *p*-type conductivity. This is a dilemma. According to our experimental data, the optimal results, resistivity of 23.7 Ω cm, carrier concentration of 3.51×10^{17} cm^{-3}, and Hall mobility of 0.752 $cm^2\,V^{-1}\,s^{-1}$, are obtained at a substrate temperature of 540 °C. The carrier concentration is high, but the mobility may not be satisfactory, especially when it comes to making *p-n* junctions and devices. Yamamoto and Yoshida[6] predicted that the codoping method would contribute to an increase in the carrier mobility due to the short range dipolelike scattering mechanism. A buffer layer can thus lead to growth of high-quality films with reduced dislocations and defects[10,11] as well as increased Hall mobility. Here, we propose a two-step growth process by introducing a buffer layer produced at a high temperature. In our experiments, a buffer layer was deposited for 7 min at 600 °C, and then the ZnO film was formed for 30 min at 540 °C on this buffer layer. Table II shows the results of the Hall-effect measurements. The mobility is observed to improve significantly even though the carrier concentration increases only slightly. It is believed that this improvement is attributed to reduced defects and dislocations that act as scattering centers for the carriers. To verify the stability of the *p*-type ZnO film, Hall-effect measurements were carried out 30 days later and no obvious degradation in the *p*-type conductivity was observed. The lowest room temperature resistivity was found to be 7.85 Ω cm for the In–N codoped *p*-type ZnO film with a buffer layer, whereas the carrier concentration was 5.40×10^{17} cm^{-3} and the Hall mobility was 1.47 $cm^2\,V^{-1}\,s^{-1}$.

In order to further understand the *p*-type behavior of In–N codoped ZnO thin films, *n*-ZnO/*p*-ZnO (~400 nm) structures were deposited on a thin ZnO buffer layer (~25 nm) on quartz. The *I-V* measurements were performed at room temperature. Figure 2 shows the *I-V* curves obtained from the Au/*p*-ZnO:(In,N)/*n*-ZnO:In/Au junction. A low turn-on voltage of 1.9 V appears under forward bias, whereas the reverse bias breakdown voltage is around 3.9 V. A low leakage current is also observed. The *p-n* homostructural diode exhibits apparent electrical rectification in our repeated measurements showing the formation of a typical *p-n* junction. The fitted curve using the equation $I = I_0[\exp(qV/\eta kT) - 1]$ is shown in Fig. 2 (open circles), where I_0 is the reverse saturation current, q is the elementary charge, k is the Boltzmann constant, T is the absolute temperature, and η is the ideality factor. A significant portion of the *I-V* curve can be fitted well using $\eta = 40$, although this η value is unexpectedly high. However, high ideality factors have been observed in other nonideal wide band-gap *p-n* junctions.[12–14] It may be caused by space-charge limited conduction, deep-level-assisted tunneling,[12] and the sum of the

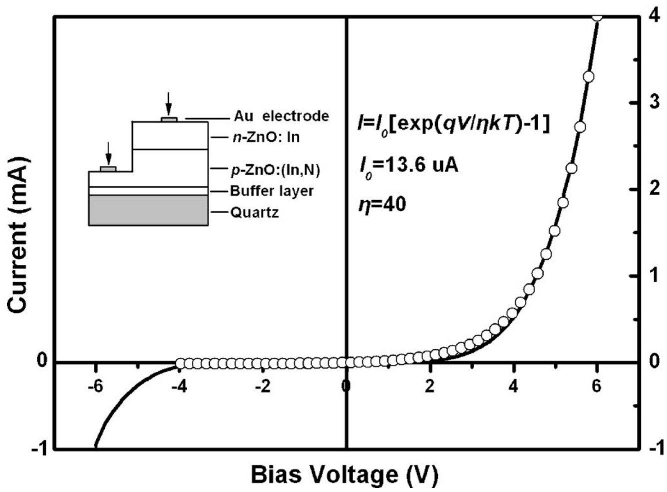

FIG. 2. *I-V* characteristic of the Au/*p*-ZnO:(In,N)/*n*-ZnO:In/Au junction (Au deposited by evaporation). The open circles show the fitted data. The inset shows the schematic diagram of this device structure.

ideality factors of individual rectifying junctions using $\eta = \Sigma_i \eta_i$, where η_i represents the ideality factor of the *p-n* junction, unipolar heterojunction, or metal-semiconductor junction.[15]

In summary, *p*-type ZnO thin films have been fabricated by In–N codoping at temperatures between 490 and 580 °C. At a lower temperature, the carrier type is ambiguous, but *p*-type conductivity is obtained at intermediate temperatures. However, the samples become *n* type at higher temperatures. The lowest room temperature resistivity of 7.85 Ω cm is found from the In–N codoped *p*-type ZnO film produced on a buffer layer. The carrier concentration is 5.40×10^{17} cm^{-3} and the Hall mobility is 1.47 cm^2 V^{-1} s^{-1}. ZnO-based homostuctural *p-n* junctions comprising a *n*-ZnO:In layer on a *p*-ZnO:(In,N) layer on a buffer layer display apparent electrical rectification in repeated measurements, thereby confirming the formation of a typical *p-n* junction. The ability to control *p*-type conductivity in In–N codoped ZnO films by adjusting the growth temperature and using a buffer layer is important to the design of ZnO-based optoelectronic devices.

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