Properties of p-type ZnO thin films with different orientations*

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The stable properties of N-doped p-type ZnO thin films with preferential nonpolar (100) plane orientation relative to polar (002) plane orientation are investigated. The two kinds of oriented thin films are fabricated by the methods of post heat treatment and double sources in situ, respectively. The Hall investigations demonstrate that N-doped p-type ZnO thin films with preferential nonpolar (100) plane orientation are more stable，and the results are also proved by build-in electric field model and electronic structure calculations of the films based on the first principle.
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ZnO is regarded as a promising material for short wavelength light emitting diodes (LEDs) and laser diodes (LDs)[1-3] due to its direct wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature[4]. But the development of the photoelectron devices has been impeded by the absence of high quality p-type ZnO for p-n junctions. It is well known that undoped ZnO generally exhibits n-type conductivity, so it is difficult to obtain p-type ZnO due to self-compensation from native donor defects and the low solubility of the p-type dopants[5]. Up to now, significant efforts have been made to produce p-type ZnO materials[6-11], and even donor and acceptors co-doped as dopants for achieving p-type ZnO thin films[12-15].

However, p-type ZnO materials are very poor in reproducibility, and the reliability of p-type ZnO is still under debate[16]. Many factors influence the stability of p-type ZnO[17], such as the kind, radius and solid solubility of doping elements, different orientations of films as well. There is almost no report on the stability of p-type ZnO thin films with different orientations[18]. In this work, we fabricated two kinds of N-doped p-type ZnO thin films oriented in preferential nonpolar (100) and polar (002) planes simultaneously by the methods of post heat-treating and double sources in situ, respectively, and then study the relationship between the stability of the p-type ZnO thin film and its orientation by experiment and theoretical calculations.

The first kind of N-doped p-type ZnO thin films were fabricated by post heat-treating n-type intrinsic ZnO thin films with preferential nonpolar (100) plane in an atmosphere of thermal-decomposing $Zn(NO_3)_2$. The n-type intrinsic ZnO thin films were fabricated on Si(100) substrates by single source chemical vapor deposition (SSCVD) technique using the precursor $Zn_4(OH)_2(CO_2CH_3)_6$ described as Refs.[19, 20] and appropriate parameter conditions of substrate temperature of 450 ℃ and chamber pressure of 10-20 Pa, which are just selected for obtaining n-type intrinsic ZnO thin films with preferential nonpolar (100) plane orientation[20]. For the purpose of achieving N-doped p-type ZnO thin films with nonpolar (100) plane, the obtained n-type intrinsic ZnO thin films were post heat-treated at 500 ℃ in an atmosphere of thermal-decomposing $Zn(NO_3)_2$. And the second kind of N-doped p-type ZnO thin films with polar (002) plane orientation were deposited on Si(100) substrates at 450 °C by the method of thermal-decomposing double sources in situ simultaneously, and the double sources are the precursor $Zn_4(OH)_2(CO_2CH_3)_6$ and $Zn(NO_3)_2$, all of which are just selected for obtaining N-doped p-type ZnO thin films with polar (002) plane orientation. The obtained ZnO thin films show nonpolar (100) plane preferential orientation and polar (002) plane orientation are named as sample 1 and sample 2, respectively. The thickness of two films is about 500 nm. In addition, two kinds of N-doped p-type ZnO thin films were also fabricated successfully at substrate temperature of 400 °C, and have properties similar to the two sample films respectively. Thus, here we only discuss the films fabricated at substrate temperature of 450 °C.

The crystalline structure properties of the two ZnO thin films are investigated using a Philips X-ray diffraction (XRD) with CuKα radiation (λ=0.15408 nm) in the θ-2θ mode. The surface chemical compositions are ana-

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lyzed by X-ray energy disperse spectroscopy (EDS) using Hitachi S-4500. And the electrical properties are examined by Hall-effect measurements using the Van der Pauw configuration (HL5500PC) at room temperature.

The electronic structure and stability of the N-doped p-type ZnO films with different orientations are first analyzed by the build-in electric field model. Then for gaining an insight into the relationship between the stability of N-doped p-type ZnO thin film and its orientation, the total electronic densities of states of the nonpolar (100) orientation N-doped ZnO ((100)ZnO:N) and polar (002) orientation N-doped ZnO ((002)ZnO:N) are calculated for qualitative analysis, which are performed by using density function theory code CASTEP[21]. The geometry of the supercell with different orientations contains six atom-layers of 32 atoms, and one of oxygen atoms is substituted by N, where the content of N in ZnO film is 3.125%. Though it is larger than the experimental value, the calculated result can also be used for qualitative analysis. Generalized gradient approximations (GGAs) are chosen for the theoretical basis of density function. The energy cutoff is set at 340 eV, and the convergence in energy and force are set at 2×10^{-5} eV and 0.5 eV/nm, respectively.

The intrinsic ZnO films in preferential nonpolar (100) plane orientation were first fabricated just under the condition selected for obtaining n-type ZnO thin films, which then were post heat-treated by $Zn(NO_3)_2$ to achieve their p-type conductivity. And the second kind of N-doped p-type ZnO thin films were also deposited simultaneously by the method of thermal-decomposing double sources in situ. Fig.1 shows the XRD patterns of the two N-doped ZnO thin films. It can be observed that they both exhibit the polycrystalline hexagonal wurtzite structural phase, sample 1 shows the strong (100) peak and relatively weak (101) and (002) peaks, while sample 2 only shows a strong (002) peak. The results demonstrate that sample 1 exhibits preferential nonpolar (100) orientation, while sample 2 exhibits polar (002) orientation.

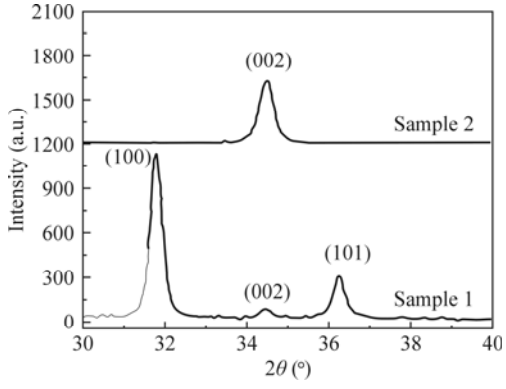

Fig.1 XRD patterns of two N-doped ZnO thin films

The surface chemical compositions of the two ZnO thin films are characterized by EDS as shown in Fig.2.

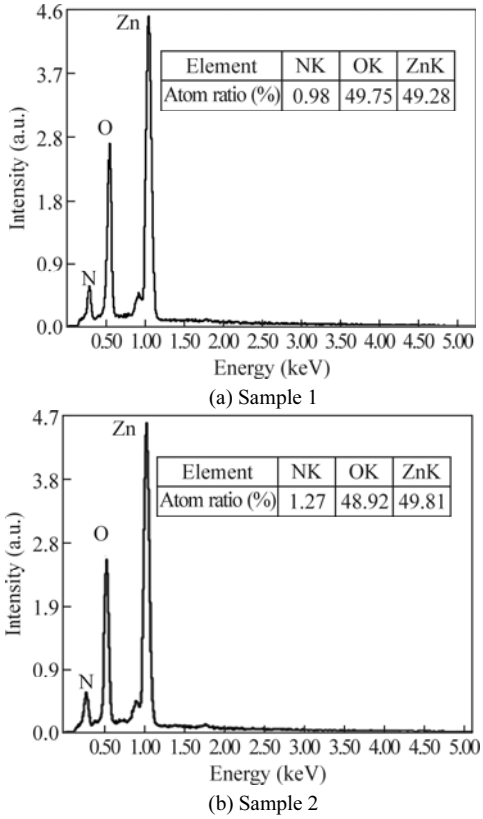

Fig.2 EDS results of surface chemical compositions of the two ZnO thin films

It can be observed that N atom is doped into the films successfully. The N atom content in sample 1 is 0.98%, and that of sample 2 is 1.27%, so there is a distinct difference from surface chemical composition between the two ZnO thin films. The content of O (49.75%) in sample 1 is higher than that of Zn (49.28%), which can be ascribed to the oxygen enrichment atmosphere during thermal-decomposing $Zn(NO_3)_2$ for sample 1 due to the possible reactions as follows:

$$Zn(NO_3)_2 \rightarrow ZnO + 2NO_2 + O_2 , \quad (1)$$

$$NO_2 \rightleftharpoons NO + O , \quad (2)$$

$$NO \rightleftharpoons N + O . \quad (3)$$

The two N-doped ZnO thin films both show the p-type conductivity, which can be considered to originate from N-doping. The hole concentration, mobility and resistivity of sample 2 are 3.17×10^{17} cm^{-3}, 8.3 $cm^2V^{-1}s^{-1}$ and 2.65 Ω·cm, respectively, while those in sample 1 are 1.57×10^{16} cm^{-3}, 7.9 $cm^2V^{-1}s^{-1}$ and 27.2 Ω·cm, respectively, which demonstrates that sample 2 shows a better p-type conductivity than sample 1. But their electrical properties investigated on the next day indicate that the conductivity of sample 2 has reversed to n-type, while that of the sample 1 has not, which is further proved by Hall measurement after a week, a month and six months. The subsequent results show that the sample 1 still exhibits p-type conductivity only with electrical parameters

varying in a range. It demonstrates that N-doped p-type ZnO thin film with preferential nonpolar (100) plane orientation is more stable than that with polar (002) plane orientation. The preferred nonpolar plane orientation favours the stability of sample 1, which is also good for the build-in electric field model analysis and electronic structure calculation of the films.

As we know, ZnO is a typical ionic compound. When Zn atom loses two electrons and offers them to O atom, Zn^{2+} and O^{2-} will form respectively. But as for ZnO thin film crystallity, it always shows polar (002) plane orientation for the lower surface free energy. The polar (002) plane can induce spontaneous and piezoelectric polarization, and the strong build-in electric field appears consequently. The schematic diagram of polar c-plane ZnO thin film crystal and its build-in electric field are shown in Fig.3.

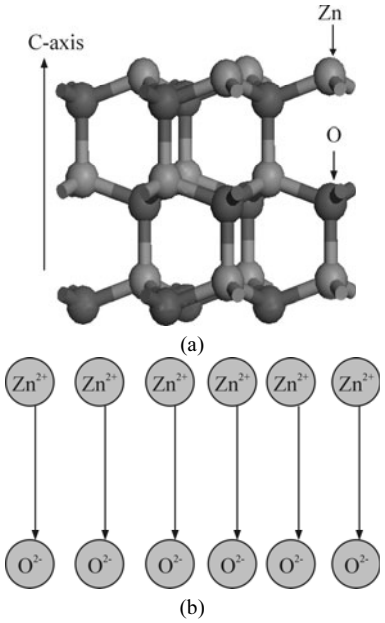

Fig.3 (a) Schematic diagram of polar c-plane ZnO thin film crystal and (b) its build-in electric field

The structure of native or N-doped p-type ZnO thin film with polar (002) plane orientation is similar to that in Fig.3. Because of the existence of the strong build-in electric field, the outer-shell electrons of O^{2-} (or N^{3-}) in ZnO film will move towards Zn^{2+} under the polar electric field forces, resulting in weakened ionic bond effect of Zn-O or Zn-N, and then a few O or N atoms may combine the vicinal O or N atoms to form O_2 or N_2, and release them from the ZnO film. So we consider that the lower stability of p-type ZnO film with (002) plane orientation originates from its polar electric field. Conversely, the p-type ZnO film grown along nonpolar direction can restrain or decrease the polar electric field. Thus the (N-doped) p-type ZnO film with nonpolar orientation is more stable than that with (002) plane orientation. The relationship between the p-type conductivity stability of the ZnO film and its orientation analyzed from the polar electric field model is consistent with the experimental results for sample 1 and sample 2.

The total electronic densities of states of (100) ZnO:N and (002) ZnO:N show that the two films both introduce an acceptor level at the top of valance bands as displayed in Fig.4. It can be seen that their valance bands show a little high energy side shift above Fermi level by about 0.3 eV, so the two exhibit p-type conductivity, which is in agreement with the experimental results. But there is an evident difference between the two conduction bands: the conduction band of electronic state of (002)ZnO:N shows a low energy side shift of about 1.65 eV compared with that of (100) ZnO:N. As we know, the state at the bottom of conduction band is mainly made up of Zn 4s orbitals. The energy of Zn 4s state in (002) ZnO:N is centered at about 2.0-6.0 eV, which is between that of zinc initial (Zn_i) (0-4.0 eV) and that of perfect ZnO crystal (4.0-7.5 eV) calculated in Ref.[22], so the Zn 4s state of (002) ZnO:N is considered to have some characteristics of Zn_i, which can be ascribed to the weakened ionic bond effect of Zn-O or Zn-N under the polar electric field forces as analyzed above. A few O or N atoms in ZnO always can combine the vicinal O or N atoms and form O_2 or N_2, then release them from the ZnO film, and some of Zn elements are left existing as Zn_i. So according to the characteristics of Zn 4s state in (002) ZnO:N, we can conclude that the p-type conductivity of (002)ZnO:N shows lower stability than that of (100)ZnO:N, which means that nonpolar (100) plane orientation is favourable to the stability of p-type conductivity.

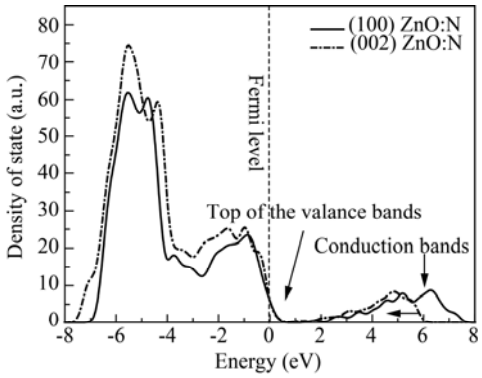

Fig.4 Total electronic densities of states of (100) ZnO:N and (002) ZnO:N

In summary, in this work, we fabricated two kinds of N-doped p-type ZnO thin films with preferential nonpolar (100) plane orientation and polar (002) plane orientation by the methods of post heat-treating and double sources in situ respectively, and study the relationship between the p-type conductivity stability of the ZnO film and its orientation by Hall measurements, the build-in electric field model and electronic structure calculation. The experimental and theoretical results both demonstrate that the N-doped p-type ZnO thin film with preferential nonpolar (100) plane orientation is more stable than that with polar (002) plane orientation, which can

provide the direction to solve the problem of p-type conductivity stability of ZnO thin films and be available for further growing high quality acceptor-doped p-type ZnO films.

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