

# Preparation and characteristics of ZnO films with preferential nonpolar plane orientation on polar sapphire substrates\*

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The properties of ZnO thin film on sapphire (0001) substrate fabricated by single source chemical vapour deposition (SSCVD) method are studied. X-ray diffraction (XRD) analysis demonstrates that the film exhibits hexagonal structures but with preferential nonpolar (100) plane orientation, which is different from the crystalline structure of substrate, and its formation mechanism is also analyzed. The film has the characteristic of p-type conductivity originating from excess of oxygen, and its p-type conductivity is comparatively stable due to its nonpolar plane orientation. A strong ultraviolet (UV) emission and a high light transmission in visible wavelength region are observed from photoluminescence (PL) spectrum and transmittance spectra at the room temperature, and the strong ultraviolet emission originates from the recombination of free and bound excitons. Compared with the ZnO film on silicon substrates, the exciton emission peaks of the film on sapphire substrate show a slight blue shift about 50 meV, which might be related to the different crystallite sizes or surface stress of the films.

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ZnO attracted considerable attention as a promising wide band-gap semiconductor for achieving shorter wavelength LEDs and highly efficient lasers. There are many deposition techniques to fabricate ZnO thin films, such as radio frequency (RF) sputtering<sup>[1]</sup>, metal organic chemical vapor deposition (MOCVD)<sup>[2]</sup>, pulsed laser deposition (PLD)<sup>[3]</sup>, molecular beam epitaxy (MBE)<sup>[4]</sup> and a novel single source chemical vapor deposition (SSCVD)<sup>[5,6]</sup>. However, undoped ZnO thin films typically exhibit n-type conductivity caused by a deviation from stoichiometry due to native defects, such as oxygen vacancies ( $V_O$ ) or zinc interstitials (Zni), which is one of the main limitations to the synthesis of p-type ZnO films, and is also accepted as the key factor in decelerating the process for the practical application of short-wavelength optoelectronic devices based on p-n junctions. Up to now, considerable efforts have been made to produce p-type ZnO thin films theoretically and experimentally<sup>[7-11]</sup>. In addition, the fabrication of ZnO thin films always shows a tendency to orient in polar (0002) plane due to its lowest surface free energy. As we know, the polar ZnO can induce the electric fields along the growth direction, and then the quantum confined Stark effect (QCSE) and poor transition probability both arise, which don't favor the light emitting device applications. Therefore, the fabrica-

tion of ZnO thin films with nonpolar plane orientation has attracted considerable attention for the application of optoelectronic device<sup>[12-14]</sup>.

In this paper, the ZnO films with preferential nonpolar (10 $\bar{1}$ 0) plane orientation are fabricated successfully on polar (0001) sapphire substrates by SSCVD using  $Zn_4(OH)_2(O_2CCH_3)_6 \cdot 2H_2O$ <sup>[15]</sup> as a solid precursor. It is found that the films fabricated at different substrate temperatures of 400 °C, 420 °C and 450 °C all exhibit intrinsic p-type conductivity, and show a high light transmission in visible (VIS) wavelength region as well as a strong ultraviolet (UV) emission originating from the recombination of free and bound excitons. But when the substrate temperature increases to 500 °C or higher, ZnO films always show polar (0002) plane orientation and n-type conductivity. According to the properties, the ZnO films with preferential nonpolar (10 $\bar{1}$ 0) plane orientation are considered to be capable of solving the problem of native n-type defect and the low luminous efficiency of the ZnO-based optoelectronic devices.

ZnO thin films were deposited on sapphire (0001) substrates by SSCVD using precursor  $Zn_4(OH)_2(O_2CCH_3)_6 \cdot 2H_2O$  in a vacuum chamber<sup>[17]</sup>. The base pressure of the chamber was set at about 20–50 Pa. The precursor was sublimed from a resistively heated Knudsen cell at a tem-

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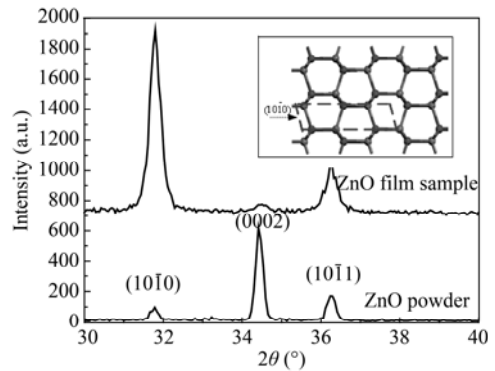
perature of 220 °C and deposited on substrates at temperatures of 400 °C, 420 °C, 450 °C and 500 °C, respectively. The deposition time was about 30 min.

The crystalline structure of the films on sapphire substrates was analyzed by a Philips X-ray diffraction (XRD) apparatus in the  $\theta$ - $2\theta$  mode, and the X-ray source is CuK $\alpha$  with a wavelength of 0.15408 nm. And the electrical properties of the films were examined by Hall-effect measurements using the Van der Pauw configuration (HL5500PC). Transmission spectra were tested by UV-VIS-NIR double beam spectrophotometer (SHIMADZU, UV-2550), and the photoluminescence (PL) properties of the ZnO thin films were characterized by IK series He-Cd laser with an excitation wavelength of 325 nm.

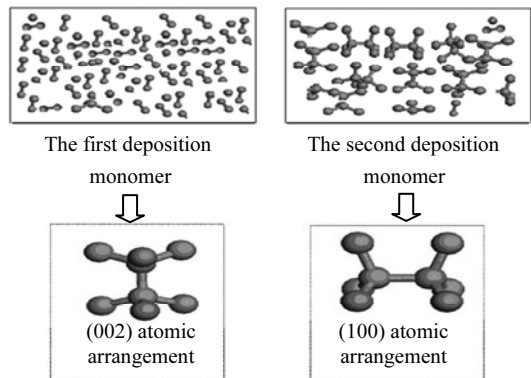
Three ZnO films deposited at different substrate temperatures of 400 °C, 420 °C and 450 °C almost show the similar characteristics of preferential nonpolar (100) plane orientation and p-type conductivity according to the investigation results, and only the film deposited at 450 °C shows a little higher carrier concentration and mobility. On the contrary, the film deposited at substrate temperature of 500 °C shows polar (0002) plane orientation and n-type conductivity. Thus, here we only discuss the properties of the films deposited at 450 °C.

The XRD of the film is performed and compared with that of ZnO powder, as shown in Fig.1. The XRD of the powder contains randomly oriented crystallites resulting in three most prominent peaks in the (10 $\bar{1}$ 0), (0002) and (10 $\bar{1}$ 1) planes. In contrast, that of the ZnO thin film shows a stronger (10 $\bar{1}$ 0) peak at  $2\theta=31.78^\circ$  and a weaker (10 $\bar{1}$ 1) peak at  $2\theta=36.23^\circ$ , while the (0002) peak almost disappears, which indicates that the film exhibits hexangular wurtzite polycrystalline structure but orients preferentially in nonpolar (10 $\bar{1}$ 0) plane. The insert of Fig.1 is schematic diagram of the atom structural model in nonplar (10 $\bar{1}$ 0) plane, where zinc and oxygen atoms are in different gray levels. It can be seen that the atom structure of nonplar (10 $\bar{1}$ 0) plane is completely different from that of polar (0002) plane with polar O-term or Zn-term surface, and the surface atom of nonplar (10 $\bar{1}$ 0) plane consists of equivalent O and Zn atoms. These demonstrate that the crystalline of the ZnO films is not the extension as that of substrates, and its nonpolar (10 $\bar{1}$ 0) plane orientation may be related to the structure of deposition monomer at the moment of thermal decomposing precursor. The possible deposition monomers always can be divided into two kinds just as shown in Fig.2. The first kind of deposition monomer consists of Zn atom, O atom and ZnO single molecular, and the second kind of deposition monomer always consists of poly-ZnO. As we know, the deposited ZnO thin films always show polar (0002) plane orientation due to its lowest surface free energy. So the first kind of deposition monomer tends to exhibit (002) atomic arrangement except for the inductive effect from crystalline structure of the substrates and other external conditions or surroundings. On the contrary, the second kind of deposition monomer tends to select (100) atomic arrangement.

Thus we consider that the nonplar (10 $\bar{1}$ 0) plane orientation of the ZnO film is related to the poly-ZnO deposition monomer. As described above, when the substrate temperature is increased to 500 °C, the deposited film exhibits polar (0002) plane orientation thoroughly, which is just ascribed to the poly-ZnO monomer's thermal decomposing and converting to the first kind of deposition monomer.



**Fig.1 XRD patterns of ZnO film sample deposited at 450 °C on sapphire substrate and ZnO powder (The inset is the atom structural model in nonplar (10 $\bar{1}$ 0) plane.)**

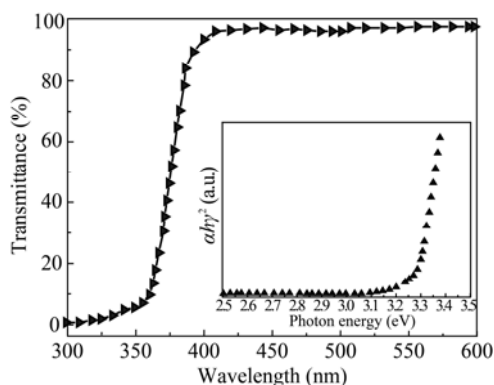


**Fig.2 Two kinds of deposition monomers and corresponding atomic arrangements**

The ZnO film sample has weak p-type conductivity determined by Hall-effect measurements at room temperature. It is a typical p-type ZnO film with resistivity of 96  $\Omega$ -cm, carrier concentration of  $4.45 \times 10^{15} \text{ cm}^{-3}$  and mobility of 14.6  $\text{cm}^2/\text{Vs}$ , and the weak p-type conductivity is attributed to the excess of oxygen in the sample film deposited under certain conditions<sup>[6,15,16]</sup>. It is more important that its p-type conductivity is comparatively stable and does not revert to n-type even over several months just as shown in Ref.[16], which might be related to the structure of nonpolar (10 $\bar{1}$ 0) plane orientation. To the best of our knowledge, the reported polar ZnO thin films with (0002) plane orientation deposited by many methods always exhibit intrinsic n-type conductivity<sup>[17]</sup>. Thus, here we consider that the correlation between nonpolar plane orientation and p-type stability is worthy of drawing attention. Although the obtained in-

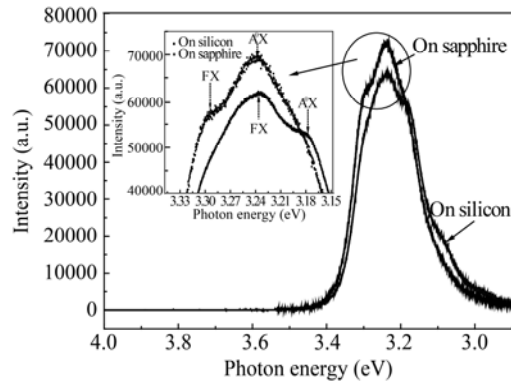
intrinsic p-type ZnO thin film has relatively low hole concentration and high resistivity, it may not be available for making high quality p-n junction devices directly. But the intrinsic defects in the films are basically suppressed by introducing self-compensation.

A high transmission over 90% in visible wavelength region can be seen from the transmittance spectra of the ZnO film sample as shown in Fig.3, but it drops sharply almost to zero when the photon energy approaches the optical band gap value. Generally, only the high quality film has the high transmission in the visible wavelength. As seen in the insert of Fig.3, the optical band gap of the film is about 3.295 eV determined by the dependence of the absorption coefficient on the photon energy, which is in good agreement with the value obtained from the PL spectra as shown in Fig.4, and that of the other ZnO film with preferential nonpolar (10 $\bar{1}$ 0) plane orientation on silicon is also shown for comparison. The strong UV band emissions of the films are both observed, and in this UV emission range, the two evident emission peaks are attributed to the recombination of free and neutral acceptor bound excitons, which are labeled as FX and A<sup>0</sup>X in the insert, respectively. As seen from the emission line of the films on the sapphire substrate, the photon energy of FX is about 3.296 eV, which is consistent with the optical band gap determined by the absorption spectra above. At its low-energy side, the emission peak of A<sup>0</sup>X centers at 3.24 eV, and the energy space between the two emission peaks is about 56 meV in both films, which indicates that the bound energy of A<sup>0</sup>X is close to 60 meV. So the A<sup>0</sup>X still exists at room temperature, which may be due to the deep level acceptor existing in the weak p-type ZnO film. In addition, it also can be seen that the exciton emission peaks of the film on sapphire show a little high-energy-side shift about 50 meV compared with that of the film on silicon, and the similar behavior originating from different substrates is also found in the study of K. H. Bang<sup>[18]</sup>. This may be ascribed to the different stresses and strain states or crystallite sizes. As we know, high intensity UV luminescence of exciton recombination is significant for the UV laser device. And just as the theory researches, the nonpolar ZnO is considered to exhibit high efficiency of UV



**Fig.3 Transmittance spectrum of ZnO film on sapphire substrate**

emission<sup>[19]</sup>, which is also confirmed by the PL spectra of the sample film. Thus the obtained p-type ZnO thin film with preferential nonpolar (10 $\bar{1}$ 0) plane orientation is significant for the application of the ZnO-based LED.



**Fig.4 Photoluminescence spectra of the ZnO thin films on sapphire and silicon (The inset shows the enlarged UV emission peaks.)**

Intrinsic p-type ZnO films with preferential nonpolar (10 $\bar{1}$ 0) plane orientation on polar (0001) sapphire substrates are successfully fabricated by SSCVD method. The formation mechanism of preferential nonpolar (10 $\bar{1}$ 0) plane orientation is analyzed. The stability of p-type conductivity is ascribed to the structure of nonpolar (10 $\bar{1}$ 0) plane orientation. Although the intrinsic weak p-type ZnO film may not be available for making high quality p-n junction devices directly, the intrinsic defects in the films are basically suppressed by introducing self-compensation. As described from the optical properties, the obtained nonpolar films exhibit strong UV band emission, which is also considered to be related to the structure of nonpolar (10 $\bar{1}$ 0) plane orientation. So the ZnO films with nonpolar (10 $\bar{1}$ 0) plane orientation may be capable of solving the problem of the low luminous efficiency of the ZnO-based optoelectronic devices. As analyzed above, it can be concluded that there is a correlation between the properties and nonpolar (10 $\bar{1}$ 0) plane orientation, which needs further studies.

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