УДК 666.3

EFFECT OF IPA VOLUME FRACTION ON PREFERRED ORIENTATION OF ZNO NANOWIRES GROWN BY CBD METHOD AND MECHANISM

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Summary. *ZnO nanowires with semi-polar and non-polar orientations are fabricated on Si (100) substrates by low temperature chemical solution deposition. This distinctive growth is achieved by a co-effect of the seed layer templates and CBD solution. The growth mechanism is illustrated in detail and these semi-polar and non-polar ZnO/Si heterostructures show an excellent unidirectional conductivity.*

ZnO nanomaterials have been widely used in optoelectronic devices, gas sensors, biosensors, solar cells and electromagnetic wave absorption due to their excellent physical chemistry properties. How to solve the C-axis predominance in the growth of nano-ZnO and prepare the semi-polar and non-polar preferred orientation has become the research focus. ZnO nanofibers were prepared by sol-gel and electrospinning methods using PVA, ethanol, acetic acid and zinc acetate dihydrate as raw materials, the effect of IPA volume fraction on the orientation of ZnO nanowires was studied by chemical bath deposition.

The precursor solution of ZnO nanowires is zinc acetate solution which is prepared by the sol-gel method. Then the fabrics of zinc acetate and PVA are obtained by electrostatic spinning, finally, ZnO nanowires is obtained by sintering in a well furnace as required. The CBD solution is formulated as follows: A 50 ml precursor CBD solution consisting of DI water and IPA as solvents which have the ratio of 40 %, 50 %, 60 %, 70 %, 80 % and 90 % (called A1–A6) with 25 mM Zn^{2+} concentration was prepared using $[Zn^{2+}]/[HMTA] = 1 : 1$ molar ratio, respectively. Afterwards, the pre-coated p-Si (100) substrates were immersed in the solution and maintained at 80 °C for 4 hours in a water bath fitted with a refluxing system.

In order to study the crystal structure of ZnO nanowires prepared by changing the volume fraction of IPA in solution, all the nanowires were tested by XRD. We calculated the texture coefficient to reflect the preference orientation of each group.

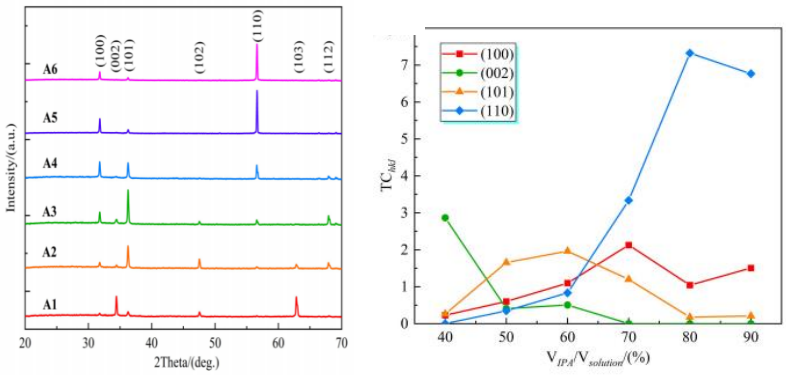

Figure 1 – Preferred orientation and crystallinity analysis of ZnO films prepared with different IPA volume fraction

The formula for calculating the texture coefficient is given as follows:

$$TC_{hkl} = \frac{\frac{I_{hkl}}{I^s_{hkl}}}{\frac{1}{n}\sum_n \frac{I_{hkl}}{I^s_{hkl}}}$$

where, I_{hkl} and I_{hkl}^{s} are the intensities of diffraction peaks of the sample and standard ICDD card corresponding to its plane (hkl).

When the texture coefficient of a crystal face (hkl) is greater than unity, the material is the preferred orientation of the (hkl) face. The higher the texture coefficient is, the higher the preferred orientation is. With the increase of IPA volume fraction, the preferential orientation of ZnO nanowires changed from (002) intrinsic growth to semi-polar surface, at last to (110) polar surface.

From the SEM images, fig. 2 (a) shows an obvious upright or inclined hexagonal prism, which is the preferred orientation of (002) .The neighboring grains are growing in competition with each other for growth space, as a result, the grains extrude each other at the place where the two grains contact to form the incomplete hexagonal morphology owing to the different orientation.The images (b) and (c) are wedge-shaped, because (b) and (c) are of the preferred orientation of (101). These grains can be seen as the inclined growth of six-prismatic grains, eventually exposed a six-prismatic angle and a row to form this wedge-shaped morphology. In fig. (d), the preferred orientation of ZnO is not obvious and it is a transition state. The fig. (e) and (f) show the "Roof-shaped" morphology of (110) preferred orientation. By forming the "Roof-shaped" morphology, the "Roof-shaped" on both sides of the grain is the (100) crystal plane of ZnO, and the plane parallel to the sample surface inside the grain is the (110) crystal plane of ZnO.

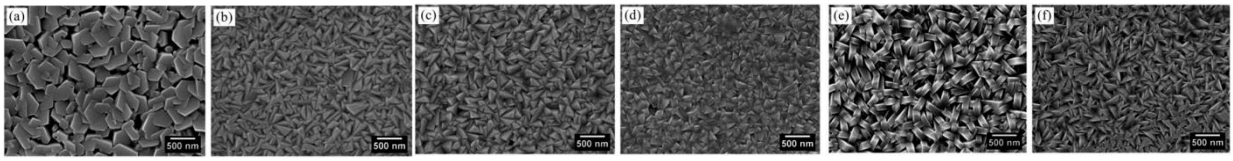

Figure 2 – The SEM images of ZnO films prepared at different IPA volume fractions:
a – 40 %; b – 50 %; c – 60 %; d – 70 %; e – 80 %; f – 90 %

The mechanism is explained from the steric hindrance effect. In solution, hydroxyl groups on IPA molecules can be linked to unbonded groups on the semiconductor surface by forming monomolecular complexes. When IPA is selectively adsorbed on a crystal face, the Steric hindrance effectis formed on above crystal face, which blocks the contact between foreign ions and the surface of ZnO, hence inhibiting the growth of the crystal face. In addition, the interaction between the functional groups of organic molecules in solution and the semiconductor surface is also affected by the polarity of the solution. The stronger the polarity of the solution, the weaker the binding force between the hydroxyl group and the unbonded group, and that being reversely. When IPA was not added, nano-ZnO was grown along the intrinsic growth surface. When the volume fraction of IPA is 40 %, the polarity of solution is still strong, the growth of (002) crystal plane is inhibited weakly. Nano-ZnO grows along (002), (103) crystal plane mainly, With the increase of IPA concentration, the polarity of solution decreases and the inhibition on (002) crystal plane is enhanced, nano-zno clearly grows along the semi-polar plane. When the volume fraction of IPA reaches 80 %, the growth of semi-polar surface is also inhibited, and nano-ZnO grows along (110) non-polar surface.

In summary, the orientation of ZnO nanowire is regulated by IPA through the Steric hindrance effect of its selective adsorption on ZnO crystal surface. Its excellent physical properties can be used in rubber, electrical properties can be used in gas sensor and humidity sensor. And because of ite adsorption, ZnO can be used to detect the protein or adsorption of pigment, too.