第 16 卷第 7 期　　半 导 体 学 报　　Vol. 16, No. 7
1995 年 7 月　　CHINESE JOURNAL OF SEMICONDUCTORS　　July, 1995

Preparation of ZnO Nanometer Powder and Their ESR Properties*

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Abstract　The preparation of ZnO nanometer powder using microemulsion method and their electron spin resonance (ESR) properties were reported. It was found that at room temperature ZnO nanometer powder has an appreciable ESR signal. It was confirmed that there are a lot of zine vacancies and defects on the ZnO particles surfaces which trap electrons and form paramagentic centers to provide the observed ESR signal.

PACC: 7630M

Semiconductor nanometer powder have been the subject of extensive researches, because they have many particular properties including quantum size effects, surface and interface effects, nonlinear optical properties and excellent photocatalytic properties[1-3]. The atoms on semiconductor nanometer powder surfaces have a larger activity, which leads to the variations of the surface atom transport property and electron spin configuration. The ESR spectrum is a powerful tool for studying the surface electron spin configuratrion and surface constructure of nanometer powder. Bulk ZnO substance is a diamagnetic material, in normal no ESR signal can be observed. While on quantum-confined-size region, we did observed ESR signal. In present paper, the ESR properties of ZnO nanometer powder under different annealing temperature were investigated. The ZnO nanometer powder are prepared through microemulsion method as fellow:

* Project supported by the Natural Science Foundation of Tianjin

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Received 8 September 1994, revised manuscript received 17 January 1995

$$Zn^{2+}\ \text{solution} \xrightarrow[\text{②toluene}]{\text{①surfactant}} \text{Mixing solution} \xrightarrow[\text{④stiring}]{\text{③}OH^-}$$

$$\text{Microemulsion} \xrightarrow[\text{⑥excluding water}]{\text{⑤circulating}} \text{ZnO microcrystal emulsion}$$

Here the surfactant can prevent ZnO particles aggregation and agglomeration. Then the ZnO emulsion was heated until the surfactant resolved completely due to being oxygenated. We can obtain pure ZnO powder with smaller size. Transmission electron microscopy and small angle X-ray diffraction exhibited its sphericle-like shape and polycrystalline structure. Figure 1 is a bright field image of the sample 1 (see last page).

The crystal sized was calculated with Scherr's formula[4], that demonstrates the particle radius is less than 10nm. Leaving 60mg power(sample 1), the other was divided into six parts (each 60mg), they were annealed separately at 200, 400, 500, 600 and 800℃ about 2 hours in SPJX-5-13 box-like electric stove, labeled them sample 2, 3, 4, 5, 6 and 7 separately. The ESR spectra were recorded on Burcker 200D-SRC spectrometer at room temperature (RT) and the results are shown in Figure 2 (see last page). When decreases the calcination temperature of powder, the intensity of ESR signal decreases. On raising the temperature to 800℃, the intensity of signal is zero.

Through composition analysis of ZnO nanometer powder, it was found that the ratio between oxygen and zine is about 2.1:1 (analysis deviation $\pm 0.03\%$)[5], which indicated that there are a lot of oxygen (O^{1-} or O^{2-}) ions on the ZnO nanometer powder surfaces which implies that electrons are trapped in the vacancies and form paramagnetic centers with oxygen ion (O^- or O^{2-}) to provide the observed ESR signal. If the ESR signal observed came from the O^- ions, then the g factor in our experiment should be equal to that of free electron g factor ($g_e = 2.0021$[6]). However from Fig. 2, we obtained $g = 2.0109 \pm 0.0003$. On the other hand, the O^{1-} ion is instabile, in general no stabile ESR signal appears. While in our experiments the ESR signals observed are stabile and very intensive at RT. Thus the O^- ion is not the paramagnetic center. However O^{2-} ions at ZnO nanometer powder surfaces are stabile and can trap electrons to form paramagnetic centers (F centers) to provide the stabile ESR signals. On the other hand, the sample's colour varies with the annealing temperature, the sample 1 appears ashen, the sample 5 (600℃) yellow, the sample 7 appears shallow yellow which is the nature colour of bulk ZnO material. It shows that increase of annealing temperature leads to increase of the particle size and reduce of interface and surface effects, so decreases of the paramagnetic centers. Above 800℃, the ZnO nanometer powder completely becomes bulk material structure behaviours, so cannot be observed ESR signal.

In order to verify above conclusions, we measured the ESR signal of ZnO nanometer powder with a lay of surfactannt (AOT) on their surfaces. Under the same condition, especially with same weight as the uncoatde ZnO nanometer powder, the ESR signal of coated ZnO nanometer powder is very weeker than that of naked ZnO powder (see last page Fig. 3).

It indicates that the surface modification can reduce the surface vacancies and defects to reduce the paramagnetic resonance centers, this phenomenon confirms that electron spin resonance centers are really on the surfaces of ZnO nanometer powder.

In summary, the microemulsion method is a simple method in preparing semiconductor nanometer powder with smaller size and stabile behaviours. Through measuring the ESR signals of nanometer powder, we can obtain some information of the microstructure of the nanometer powder even for those materials exhibiting diamagnetism in normal state.

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