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Photoluminescence investigation on the gas sensing property of ZnO nanorods prepared by plasma-enhanced CVD method

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ABSTRACT

Gas sensing property of ZnO nanorods prepared by plasma-enhanced chemical vapor deposition (CVD) method is studied using formaldehyde as the probe gas, and the intrinsic defects are investigated by photoluminescence (PL). The results show that high ratio of visible to ultra-violet luminescence cannot account for high gas response. The PL spectra are Gaussian decomposed to subpeaks according to their origination, which are separated into donor- (DL) and acceptor-related (AL) ones. A conclusion is derived that where the content of DL is high and that of AL is low, the gas response is high. This conclusion is further confirmed by tuning the PL spectra and gas sensing property through annealing in different atmospheres.

1. Introduction

Since the first application in gas sensor [1], ZnO has found its way in explosive gas alerting and toxic gas detection for decades, with various morphologies and different dopants contributing much to the development of resistance-based ZnO gas sensors [2,3]. But the key factor determining the gas sensing property of ZnO is still under debate. The most prevalent model is founded using SnO_2 by Xu et al. [4] that compares the particle diameter (D) and depth of surface charge layer (L): if D is comparable to or less than $2L$, the gas response is expected to be high. However, just comparing D and L leads to dilemma in some studies [5–7], because L is hard either to be measured or to be calculated.

As the electronic property of ZnO mainly depends on its intrinsic defects [8], the gas response defined as the ratio of resistance in air and in detectant (R_a/R_g) is therefore closely correlated to the intrinsic defects [9,10]. Photoluminescence (PL) spectra is the luminescences originated from the photo-induced electron/hole and/or the intrinsic defects in ZnO [8]. Therefore, there are several defect-related luminescences as well as the photo-induced near band edge excitation in ZnO PL spectra. Thus some researchers used the intensity ratio of visible luminescence to ultra-violet luminescence (I_{VL}/I_{UL}) to evaluate the crystallinity of ZnO crystal: the higher the ratio, the more the intrinsic defects [10,11]. However, Shi et al. [12] pointed out that the ratio of I_{VL}/I_{UL} is affected by sample type as well as excitation density, and could not be simply used to assess the crystal defects. Therefore, we tried to use decomposed PL spectra to distinguish donor-related (DL) and acceptor-related luminescences (AL) and further to investigate the relationship between the intrinsic defects and the gas sensing property of ZnO.

The ZnO nanorods with different lengths used here are prepared in seconds by plasma-enhanced chemical vapor deposition (CVD) method under high temperature and thus possess lots of intrinsic defects [13,14]. Furthermore, the defects were tailored by annealing in different atmospheres and the relationship between the intrinsic defects measured by PL and the gas sensing property of ZnO was confirmed. It should be noted that the donors and acceptors in ZnO crystal play different roles in electron transport, and they affect the gas sensing property of ZnO in opposite way.

2. Experimental

2.1. ZnO nanorods preparation

The ZnO nanorods were prepared by RF thermal plasma-enhanced CVD method as we reported earlier [13]. Briefly, zinc powder and oxygen were introduced into the Argon plasma (30 kW, 4 MHz), after a vapor-solid (VS) growth process and with a two-directional growth mechanism, the ZnO nanorods were gained. The

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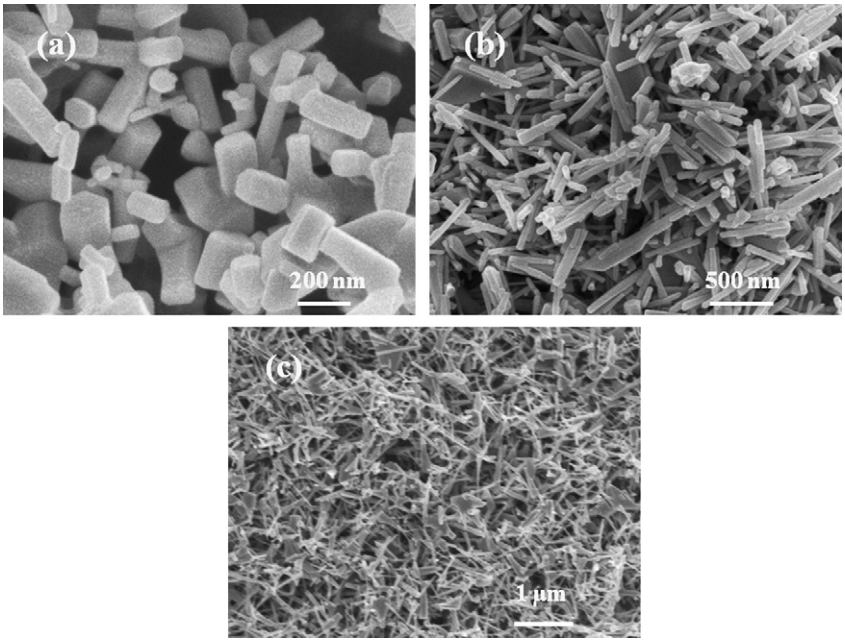

Fig. 1. SEM images of (a) ZnO200, (b) ZnO500 and (c) ZnO2k.

morphology of final product could be well controlled by adjusting the ratio of oxygen partial pressure (oxygen flow rate). The three samples used herein are: 200 nm, 500 nm and 2000 nm in length respectively, with similar sectional diameter of 50–100 nm (denoted as ZnO200, ZnO500 and ZnO2k), as observed by scanning electron microscopy (SEM, JSM-6700F) in Fig. 1.

In the post annealing treatment, the ZnO samples were placed in Al_2O_3 boats in a tube furnace (inner diameter 45 mm) at required temperature for 2 h. For air annealing, the tube was open to atmosphere, while for H_2, N_2 and O_2 annealing, these gases were introduced into the sealed tube at a velocity of 100 ml min^{-1}.

2.2. Characterization

The gas sensing property was tested in a home-made instrument as we reported earlier [15,16], and the gas response is defined as R_a/R_g, where R_a and R_g are the resistance of the sensor in air and in detectant. The Raman spectra were measured on Horiba Jobin Yvon LabRAM HR800 Raman Microscope (514 nm Argon laser, 20 mW, France). And the PL spectra were recorded from 350 nm to 800 nm at room temperature by a 325 nm excitation from Xe lamp (Perkin Elmer LS 55 fluorometer).

3. Results and discussion

3.1. As-prepared ZnO nanorods

It is reported that nitrogen might be incorporated into the ZnO crystal by high temperature annealing of ZnO in N_2 atmosphere [17], and so might do in plasma-CVD system (about thousands degree). In N-doped ZnO, there are additional Raman shift peak at ~510 cm^{-1} and 643 cm^{-1} [18], besides the ZnO peaks of E_{2L} (~100 cm^{-1}), A_{1T} (~380 cm^{-1}), E_{1T} (~410 cm^{-1}), E_{2H} (~438 cm^{-1}), A_{1L} (~574 cm^{-1}) and E_{1L} (~584 cm^{-1}) [19]. But actually, only $3E_{2L}$, A_{1T}, E_{1T}, and E_{2H} peaks were observed in the Raman spectra of the three ZnO nanorods, as shown in Fig. 2, with no Raman shift peak related to N-dopant observed. And no XRD peak related to Zn_3N_2 was detected in our previous study [13]. So, we can rule out the extrinsic defect (N-dopant), and are concentrated on the gas sensing property investigation of pure ZnO nanorods.

The formaldehyde gas sensing property of the ZnO nanorods at 300 °C and 400 °C, where the gas sensing property is high according to the literature [2,3,15], are tested as shown in Fig. 3. We can see that ZnO500 performed the highest gas response at both 300 °C and 400 °C, followed by ZnO200 and ZnO2k. This result is hard to explain from the viewpoint of the widely accepted model that compares D and L [4], because the material used herein is not particles

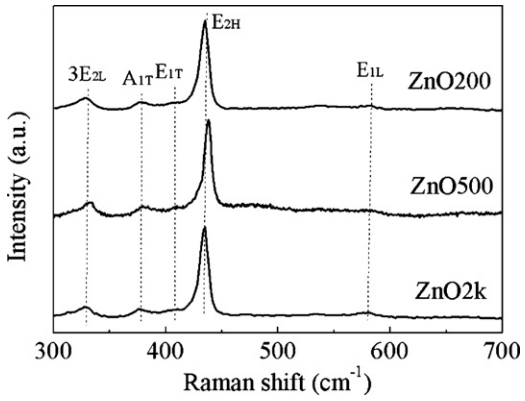

Fig. 2. Raman spectra of ZnO nanorods.

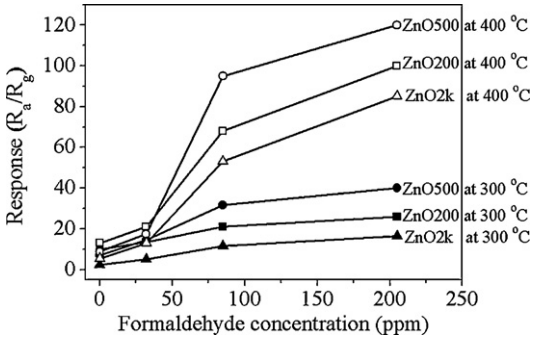

Fig. 3. Formaldehyde response of the ZnO nanorods (tested at 300 °C and 400 °C at RH 70%).