INVESTIGATION OF ZnO NANO STRUCTURES FABRICATED ON AL₂O₃ SUBSTRATES BY MOCVD

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ABSTRACT

High quality ZnO nanostructures were grown directly on sapphire substrates by metal organic vapor deposition. By changing the growth conditions, the different nano structures (nanorods, nanotubes, nanowalls, nanonetworks) can be selectively. These nanostructures were all epitaxially grown and had the same epitaxial relationship with respect to the substrate. Mechanisms corresponding to different nanostructures were discussed. The nanostructures exhibited stable excitonic states at room temperature, and the emission due to exciton-exciton scattering was observed.

1. INTRODUCTION

Semiconductor nanostructures have drawn great interest recently due to their strong application potentials as components for nanoscale electronic or optoelectronic devices exploiting superior optical and electrical properties [1, 2]. Nanostructures based on wide-gap semiconductors such as GaN and ZnO are of particular interest because they are promising candidates for short-wavelength photonic devices and high-power, high-frequency electronic devices. ZnO is characterized by a direct band gap of 3.37 eV at room temperature and a large exciton binding energy (60 meV), which is much larger than that ~25 meV of GaN and thermal energy at room temperature. This makes excitonic states stable, and exciton-involved light-emitting processes, which enable the fabrication of high efficiency photonic devices, are possible at room

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temperature. Nanocrystalline or polycrystalline ZnO can also be used in many kinds of devices such as surface acoustic wave devices, transparent electrodes, transparent thin film- transistors, varistors, solar cells, and sensors.

Many growth techniques have been used to synthesize various kinds of ZnO nanostructure and a review has been given by Dai *et al.* For example, it was for radiofrequency (RF) magnetron sputtering, molecular beam epitaxy (MBE), and metal organic chemical vapor deposition (MOCVD).

The reported ZnO nanostructures include nanorods, nanowires, nanobelts, nanonails, nanobridges, nanopins, nanodots, nanoflowers, and quantum wells. In ZnO quantum wells, the binding energy of excitons and biexcitons has been shown to be enhanced significantly. The binding energy of biexcitons can become comparable to the thermal energy at RT, indicating the possibility of realization of practical biexciton-based light-emitting devices. In nanorods or nanowires, lasing action based on exciton-exciton scattering has been observed [3], and biexciton emission has been demonstrated to be stable up to 200 K. In addition, ZnO nanorods and nanopins have been demonstrated to be applicable to field-emission devices. A quantum confinement effect has also been observed from ZnO quantum dots grown on SiO₂ using MOCVD. These results suggest the importance of ZnO nanostructures in applications of nanoscale photonic and electronic devices. The combination of various nanostructures is of great interest in developing advanced nanoscale photonic and electronic devices.

MOCVD has been demonstrated to be an effective technique for the formation of well-aligned ZnO nanorods [4]. It has various advantages: it enables the crystal growth at low temperatures (400 - 500°C), it does not require a catalyst and formation of exact hexagonal rod shapes and epitaxial growth is possible.

In this paper, a different approach for synthesizing ZnO nanostructures like nanorods, nanowalls, nanotubs, and nanonetworks is described. The surface morphology, structural and optical properties of ZnO nanostructures are investigated.

2. EXPERIMENT

The MOCVD system is the same as that used in our previous study [5]. A system with a horizontal rectangular stainless steel (SUS304) chamber (300 mm × 3110 mm × 390 mm). To prevent the pre-reaction, DEZn was conducted to the substrate surface using a stainless nozzle. On the other hand, O₂ was introduced by two pathways. A part of the O₂ flow was directly conducted to the substrate surface using a stainless nozzle and the remaining O₂ flow was introduced through an inlet that is about 100 mm large in front of the substrate. The chamber pressure was controlled using a conductance valve. The substrate was put on a susceptor (Inconel 600) that was heated by halogen lamps. The lamps were put beneath a quartz window opened at the bottom of the chamber. The oxygen gas (O₂, purity 99.99995%) and diethyl zinc (DEZn, Zn(C₂H₅)₂, purity 99.999%) were used as precursors and the nitrogen gas (N₂, purity 99.9999%) was used as the carrier gas for DEZn. Al₂O₃(11 $\bar{2}$ 2) and Al₂O₃ (1000) substrates (lattice constants: $a = 54.75 \text{ \AA}$, $c = 513.00 \text{ \AA}$) were cleaned in an ultrasonic bath of organic solution and then placed in the reactor. At room temperature, O₂ flow was started then the substrate was heated to 400 - 500°C and DEZn was introduced to start the growth. During the growth the flow rates of O₂ and N₂, reactor pressure was kept at constant values appropriately to get a ZnO nanostructure respectively. The surface morphology was examined using a field-emission scanning electron microscope (FE-SEM, JOEL, JSM-6330F), an atomic force microscopes (AFM - Seiko Instruments, SPA300). X-ray diffraction (XRD) measurements were carried out using a triple-axis, four-crystal Philips Expert diffract meter. The optical properties of the films were investigated by photoluminescence (PL) spectroscopy at 4.2 K and room temperature using either the 325 nm line of a He-Cod laser or the fourth harmonic (266 nm) of a

Nd:YAG (LOTIS TII, RS-2138) with a pulse width of 15 ns and a repetition rate of 50 Hz laser as the excitation source. The emission from the sample was conducted to a spectrometer (SP300- Acton Research); focus length 30 cm! and detected using a charge coupled device.

3. RESULTS AND DISCUSSION

Figure 1 shows SEM images of ZnO nanostructures on sapphire substrates under various values of pressure growth (P_v) and temperature growth (T_g). ZnO nanowalls, nanotubes, nanosheets nanorods were obtained at pressure of 0.01 - 0.1; 0.1 - 0.6; 5 - 10 torr and temperature about of 400 - 450°C respectively.

Fig. 1: SEM images of ZnO nanostructures growth under different pressure: a: 0.06; b: 0.6; c: 1; d: 3; e: 6 torr on $\text{Al}_2\text{O}_3(0001)$ and f: 6 torr on $\text{Al}_2\text{O}_3(11 - 20)$ Substrate

The nanowalls had a thicknesses of 50 - 100 nm (Fig. 1a), P_v increase to 0.3 and 0.6 torr the ZnO hexagonal cylinder take form with the diameters and wall thickness of the tubes were about 500 and 100 nm, respectively, all the hexagonal nanotubes had the same in-plane orientations (Fig. 1b). P_v increase to 1 - 3 Torr ZnO like nano particles or nanosheets further increase of P_v to 6 and to 10 torr nanorods formed with diameter is about 500 nm (on $\text{Al}_2\text{O}_3(0001)$ substrate) and 30 to 100 nm (on $\text{Al}_2\text{O}_3(11\bar{2}2)$) substrates. The formation of ZnO nanostructures can get on $\text{Al}_2\text{O}_3(0001)$, $\text{Al}_2\text{O}_3(11\bar{2}2)$ substrates but the density of the nanowalls and nanotubes on $\text{Al}_2\text{O}_3(0001)$ is higher than that on $\text{Al}_2\text{O}_3(11\bar{2}2)$ in the same condition growth. However, the diameter of the rod which grew on $\text{Al}_2\text{O}_3(11\bar{2}2)$ is smaller than that grew on $\text{Al}_2\text{O}_3(0001)$ and at high temperature growth some rods are connected together by walls- that is nanonetworks Fig. 1f). The influence of the growth condition on morphology is shown in table 1.

The XRD results demonstrated that all nanostructures grew with C-axis parallel to the normal substrate surface. This is because the top (0001) surface has the lowest level of surface energy and, in an equilibrium state, the crystal grows with this plane parallel to the substrate surface. Figure 2(a) shows Φ scan spectra of ZnO(11 $\bar{2}2$) planes of different nanostructures along with those of sapphire (11 $\bar{2}2$) planes. Six peaks with equal 60° intervals were obtained from all of the nanostructures, though they have different shapes, and their peaks are shifted 30° from those of the substrate. It is thus clear that ZnO nanorods, nanotubes, and nanowalls are all grown epitaxially and have the same epitaxial relationships with respect to the substrate. XRD rocking

curves of ZnO (0002) crystal planes obtained from nanorods, nanotubs, nanowalls. The fullwidth- at-half-maximum (FWHM) values are from 0.47° , 1.68° , 0.64° to 2.1° , indicating that all of the nanostructures were grown with good alignment.

Table 1. ZnO nanostructures at different growth conditions

Structure	Substrate	Temperature growth ($^\circ\text{C}$)	Pressure (Torr)	Gas flow (ccm)	
				O ₂	N ₂
Nanowalls	Al ₂ O ₃ (0001), Al ₂ O ₃ (11 $\bar{2}2$)	400 - 450	0.03 - 0.1	30	6
Nanotubes	Al ₂ O ₃ (0001), Al ₂ O ₃ (11 $\bar{2}2$)	400 - 450	0.3 - 1	30	6
Nanorods	Al ₂ O ₃ (0001), Al ₂ O ₃ (11 $\bar{2}2$)	400 - 450	6 - 10	30	6
Nanonetworks	Al ₂ O ₃ (11 $\bar{2}2$)	475 - 500	6 - 10	30	6

Fig. 2: Φ scans of the (11 $\bar{2}2$) family of planes of ZnO, (11 $\bar{2}6$) of sapphire substrates (a) and typical XRD rocking curves (a) of ZnO (0002) planes of different nanostructures. In both panels a and b, the growth pressures were (i) 0.06, (ii) 0.3, and (iii) 6 Torr, corresponding to nanorods, nanotubes, and nanowalls, respectively. In panel b, dotted curves are measured results and solid ones are fitted results, using Gaussian profiles.

Photoluminescence (PL) measurements were carried out at 4.2 K using a He–Cd laser with an excitation wavelength of 325 nm. Figure 3 shows the low temperature PL of different ZnO nanostructures obtained when change pressure growth.

The spectra are displayed in the order of decreasing pressure growth from 10 (top) to 0.06 Torr (bottom) corresponding to the structure change from nanorods to nanowalls. The peak at 3.366 eV is common to all nanostructures (or all values of P_v) and is attributed to neutral-donor-bound excitons (D^0X). In addition, a few peaks were observed depending on the P_v value or the nanostructure. The origin of the peak at 3.333 eV, observed when $P_v = 0.6 - 10$ Torr, may be due to acceptor bound excitons. The peak located at 3.312 - 3.318 eV is due to donor-acceptor

pairs (DAP) with an acceptor binding energy of 107 meV or 124 meV. A general trend is that the DAP to- D^0X intensity ratio becomes larger with a decrease in P_v . This indicates that the growth at lower pressure in MOCVD may enhance the incorporation of acceptors in ZnO. The spontaneous doping of nitrogen, which is known to act as an acceptor, might have taken place in these structures. At high temperature growth (475 - 500°C) ZnO have nanorods or nanonetworks structure, in PL spectrum the green band disappear 3.3604 eV, and biexcitons denoted by M at 3.3571 eV and a free exciton at 3.3777 eV appear. The linewidth of D^0X is 1 meV and 0.7 meV with ZnO nanorods growth on $Al_2O_3(0001)$ and $Al_2O_3(1\bar{1}\bar{2}2)$ respectively, which is comparable to that of bulk 0.7 meV. This value is much smaller than the reported values from ZnO epitaxial films 1.5 - 4.8 meV, clearly indicating that the ZnO nanorods have good optical qualities.

Fig. 3: Low-temperature PL spectra of different nanostructures. The peaks at 3.366 and 3.312-3.318 eV are due to D^0X and DAP, respectively. With a reduction in the growth pressure, the DAP-to- D^0X intensity ratio becomes larger, which suggests an increased acceptor concentration (a), and low temperature PL of ZnO nanorods growth at 475°C (b)

Fig. 4: PL spectra under different excitation powers of the third harmonic of a Nd:YAG laser. The inset shows the emission intensity of the emission line due to exciton-exciton scattering as a function of excitation power

Under the excitation of the third harmonic of a Nd:YAG laser (355 nm; pulse width, 15 ns; repetition rate, 50 Hz), a stimulated emission was observed from samples of ZnO nanorods and nanonetworks. At low excitation intensity, only a broad peak (FWHM, 0.11 eV) due to a spontaneous emission was observed. When the excitation intensity exceeds a threshold, a sharp peak emerged at 3.205 eV. This peak is attributed to exciton-exciton scattering and assigned as P2. When the excitation intensity is increased, this peak shifted to 3.190 eV (denoted by P) in which the exciton was scattered to the continuum state. *P* line is attributed to exciton-exciton scattering.

4. CONCLUSION

ZnO nanostructures: nanorods, nanotubes and nanowalls were selectively obtained by controlling the reactor pressure and temperature in growth by MOCVD. These nanostructures were all epitaxially grown and had the same epitaxial relationship with respect to the substrate. The growth at lower pressures was found to enhance the incorporation of acceptors in ZnO, which gives guidance toward the realization of p-type, the growth at high pressure and high temperature was found emission due to exciton-exciton scattering in nanorods and nanonetworks opening potential applications of these nanostructure networks in nanoscale photonic devices

REFERENCES

1. Özgür, Ü., Alivov, Ya.I., Liu, C., Teke, A., *et al.* (2005), J. Appl. Phys., vol. 98, p. 041301.
2. Zhang, B.P., Wakatsuki, K., Binh, N.T., Segawa, Y., and Usami, N. (2004), J. Appl. Phys., vol. 96, p. 340.
3. Tang, Z.K., Wong, G.K.L., Yu, P., Kawasaki, M., Ohtomo, A., Koinuma, H., and Segawa, Y. (1998), Appl. Phys. Lett., vol. 72, p. 327.
4. Binh, N.T., Bao-Ping ZHANG, Liu, C.Y., Wakasuki, K., *et al.* (2004), J. Appl. Phys., vol. 43, p. 4110.
5. Zhang, B.P., Binh, N.T., Segawa, Y., *et al.* (2004), Appl. Phys. Lett., vol. 84, p. 586.