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Catalyst-free pulsed-laser-deposited ZnO nanorods and their room-temperature photoluminescence properties

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ZnO nanorods with various diameters were synthesized on both sapphire and silicon substrates by a pulsed-laser-deposition technique without a catalyst using relatively high background oxygen pressure (5–20 Torr) and substrate temperature (550 °C-700 °C). The photoluminescence (PL) properties of the nanorods were investigated. The difference in PL emission intensity for the samples produced at various oxygen pressures has been attributed to the size difference and surface status of the nanorods. The increased deep level emission with increasing temperature resulted from the size difference and increasing oxygen evaporating. The effect of substrate nature on the PL property has also been investigated. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2168675]

ZnO is a wide band-gap semiconductor and is of interest in electro-optically functional devices.[1] The optical properties of the nanostructured ZnO have attracted plenty of attention due to their size- and shape-dependent optical response. At present, the ZnO nanowires and nanorods are mainly synthesized by chemical or physical vapor deposition technique with a catalyst and few reports are based on pulsed-laser deposition (PLD). On the other hand, PLD has been found a powerful technique to produce high-quality ZnO films, most of which were prepared under a relatively low oxygen pressure (<1 Torr).[2] Recently, $Mg_xZn_{1-x}O$ nanowires have been synthesized on Au-covered sapphire substrate by a high-pressure PLD technique.[3] Ga-doped ZnO nanorods were grown on an α-plane sapphire and an epitaxial GaN (0002) film by PLD at an oxygen pressure of 10^{-2} Torr, but no nanorod was found for the undoped ZnO.[4] Kawakami *et al.*[5] synthesized ZnO nanorods with 300 nm diameter by PLD under 5–10 Torr oxygen pressure at 700 °C. Sun *et al.*[6] claimed that they had grown ultrathin needle-like ZnO nanorods on Si substrates using catalyst-free PLD at a low pressure ($\sim$10 mTorr). However, few investigations were based on the size control of the nanorods produced by PLD.

The room temperature photoluminescence (PL) spectrum for ZnO usually shows three major peaks: a UV near-band-edge emission peak around 380 nm, a green emission peak around 520 nm, and a red or orange emission around 600 nm.[7–11] The two broad visible bands are generally attributed to deep-level defects in a ZnO crystal, such as vacancies and interstitials of zinc and oxygen. In general, the PL spectrum of powder or polycrystalline thin film shows much stronger deep-level emissions than UV emissions, while the epitaxial thin films on lattice-matched single-crystalline substrates show weaker deep-level emissions because of the reduced structural defects.[8,9]

In this work, we synthesized the ZnO nanorods with various diameters by PLD at the relatively high background pressure of 5–20 Torr and substrate temperature 550 °C–700°C without a catalyst. The PL properties of the nanorods produced by various processes have been investigated.

A sintered ZnO target (99.99%) was ablated in an oxygen background over the pressure range 0.25–20 Torr by a KrF excimer laser with a fluence of $\sim$250 mJ. Nanostructured ZnO were deposited on the (006) sapphire or (001) silicon substrates heated up to 780 °C. The target-substrate distance was adjusted from 42 to 20 mm responding to the reduced plume length due to increasing background pressure. The crystallographic property of the nanorods was described by x-ray diffraction (XRD) (Philip 1710, Cu-$K\alpha$). The morphological property was obtained by Field Emission SEM (JEOL JSM-6700F). The PL spectra were examined by a Renishaw spectrophometer using a 325 nm Hd-Cd laser as the excitation light source.

XRD spectra (not shown here) for all samples mainly showed strong $(00l)$ peaks ($l=2$, 4, 6, etc.), indicating that produced ZnO were c-axis oriented and the background pressure in the range 5–20 Torr and substrate temperature in the range 550 °C-700 °C have no significant effect on the growing direction of the ZnO grains. Figure 1(b) shows the top view and cross section of the ZnO nanorods produced at 700 °C and 10 Torr on a sapphire substrate. Reducing the pressure down to 5 Torr led to a reduced mean diameter of the nanorods [Fig. 1(a)]. When the pressure was increased to 20 Torr, the mean size increased significantly and the nanorods started to contact each other [Fig. 1(c)]. A continuous film will be formed when the pressure is further increased. On the other hand, the ZnO synthesized at the pressure <5 Torr were also found to be continuous films. The results indicate that the high oxygen pressure is very important to grow well-aligned ZnO nanorods, which is in good agreement with the conclusion drawn from chemical vapor-deposited ZnO nanorods by Liu *et al.*[12] Figure 1(d) shows a ZnO array deposited at 10 Torr and 600 °C. The hexagonal nanorods are isolated from each other and have a mean diameter of $\sim$180 nm, in comparison with $\sim$400 nm for those obtained at 700 °C [Fig. 1(b)]. The ZnO array obtained at 550 °C is covered by the hexagonal crystals with a mean size of $\sim$120 nm. It was found that, in the temperature range

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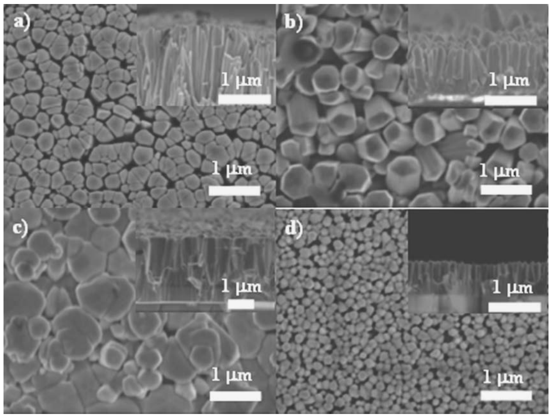

FIG. 1. Top-view and cross-section (inset) images of ZnO nanorods prepared at various background pressures and substrate temperatures: (a) 5 Torr, 700 °C, (b) 10 Torr, 700 °C, (c) 20 Torr, 700 °C, and (d) 10 Torr, 600 °C.

550 °C-700 °C, the nanorod diameter decreased with decreasing temperature. When the temperature was less than 500 °C or higher than 750 °C, no nanorod could be formed and continuous film was obtained. The detailed investigations on the effects of the PLD parameters on the nanorod size will be presented on a separated paper.

Thus, *c*-axis oriented ZnO nanorods were easily synthesized on the sapphire substrate by the laser ablation technique without using a catalyst. The size control can be accomplished by adjusting the temperature and pressure in the range of 550 °C–700 °C and 5–20 Torr, respectively. Using similar experimental conditions, the ZnO nanorod can also be fabricated on the silicon substrate. Figures 2 show the ZnO arrays on Si substrates fabricated at 10 Torr and various temperatures. The nanorods synthesized at 550 °C and 600 °C have the mean diameters of ~300 nm and ~400 nm, respectively.

PL measurements for the ZnO nanorod arrays obtained at various processes were performed at room temperature. Figure 3 shows the spectra of the nanorods deposited on a sapphire substrate with a fixed temperature of 700 °C and at various pressures. Each spectrum shows a luminescence emission at an UV wavelength, peaking at approximately 380–385 nm, which is known to be due to the direct recombination of excitons. We noticed a shoulder on the UV emission peak for nanorods obtained at 5 or 20 Torr, which is likely due to surface excitons, expected for samples with a small grain size.[13] Also, this shoulder seems to response to the various rod sizes, as shown in Fig. 1(b). Thus, the appearance of one UV peak for nanorods obtained at 10 Torr may be an indication of uniform distribution of the rod size. Some previous work seems to support this result.[14,15]

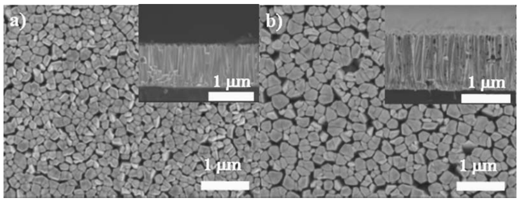

FIG. 2. Top-view and cross-section (inset) images of ZnO nanorods deposited on 550 °C (a) and 600 °C (b) silicon substrates at 10 Torr background pressure.

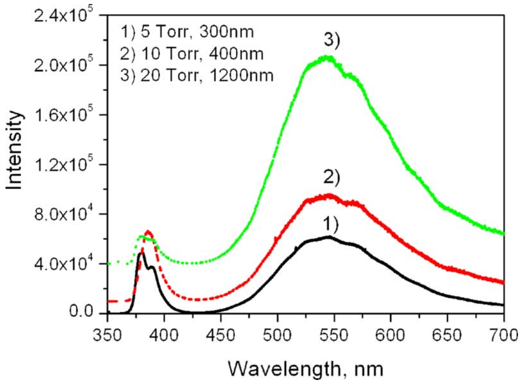

FIG. 3. (Color online) PL spectra of ZnO nanorods deposited on sapphire substrate at a fixed temperature of 700 °C and various pressures.

In Fig. 3, each spectrum also shows a wide and strong peak at ~550 nm, responding to the green emissions. Though the interpretation of the deep-level emissions, i.e., the green and red emissions, is still controversial because of complicated microscopic defects in ZnO, it is generally accepted that the deep-level emissions are closely related with structural defects such as oxygen vacancies or zinc interstitials.[10,11] Figure 3 shows that, with reducing oxygen pressure from 20 to 5 Torr, the deep-level emission intensity decreases and the intensity ratio of UV to deep-level emission even decreases further. This is surprising because one may expect a reduced deep-level emission with increased oxygen pressure since the quantity of the oxygen vacancy is expected to decrease. The reason, in our opinion, can be attributed to the size difference and surface status of the nanorods. For the nanoscale structures, the effect of the surface status on the PL intensity must be carefully considered, and the particle boundaries must be taken into account.[16,17] Band bending will create an electron depletion region at the ZnO rod surface of width W, which is up to more than 100 nm.[18] In this region, all oxygen vacancies will be in the diamagnetic doubly ionized $V_O^{\bullet\bullet}$ state. As we know, only paramagnetic singly ionized $V_O^{\bullet}$ is responsible for the green emission.[19] This surface layer plays an important role in the PL process, as the photoemissions can occur only in the central region of the ZnO nanorods, deep from the surface. Hence, for the nanorods with a larger diameter, where the depletion layer is not so important, the oxygen vacancies in the nanorod center lead to stronger green emission, but for the nanorods with small diameters, the volume of the depletion layer is a large portion of the total volume of the rod, and this layer reduces the green emission intensity. Therefore, as shown in Fig. 3, increasing the rod diameter with increasing background pressure leads to an increased intensity of green emission. The PL spectrum for the nanorods fabricated at 20 Torr is very similar to that observed for continuous films on a sapphire substrate by PLD, in which the green band emission dominated.[20] It indicates the PL of the nanorod array is similar to continuous film once the nanorods are getting thicker and contact each other. The results thus imply that our nanorods were still oxygen deficient though they were produced at relatively high oxygen pressures. The reason may be attributed to a relatively high deposition temperature (700 °C), as discussed later.

The PL spectra for ZnO nanorods deposited on sapphire substrate at 10 Torr and various temperatures are shown in Fig. 4. In the range 550 °C-700 °C, the nanorods obtained at

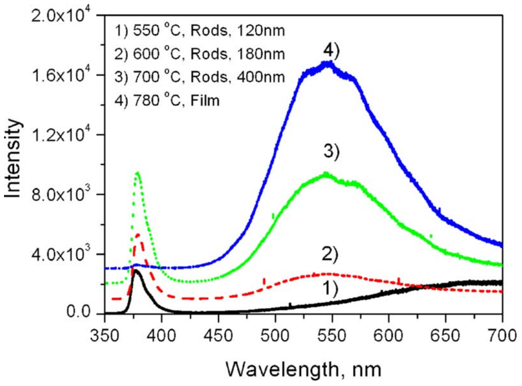

FIG. 4. (Color online) PL spectra of ZnO nanorods deposited at 10 Torr background pressure on a sapphire substrate heated to various temperatures.

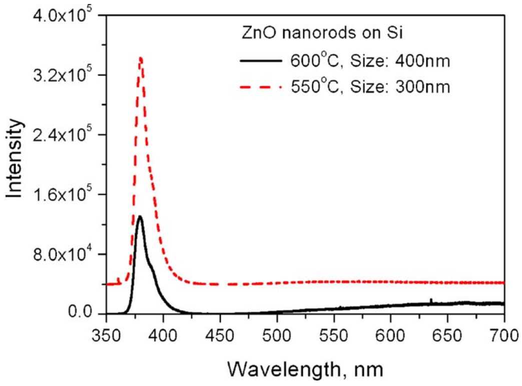

FIG. 5. (Color online) PL spectra of ZnO nanorods deposited at 10 Torr background pressure on silicon substrate heated to various temperatures.

lower temperatures have a higher ratio of UV to deep-level emission intensities. When the temperature goes up to 600 °C-700 °C, the deep level emission starts to get higher and dominates the PL spectrum. The reason, again, can be attributed to the size difference. Meng *et al.*[21] also attributed this behavior to the competition between the O atoms getting into the lattice and those evaporating out of the ZnO lattice in an O_2 atmosphere. At a lower temperature, the kinetic energy of atoms in the ZnO lattice is relatively low and the absorption rate of the O atoms is faster than the escaping rate, so more O atoms can compensate the O vacancies. But at higher temperatures, the kinetic energy of the atoms becomes larger, possibly resulting in a larger escaping rate of O atoms than the absorption rate to make more O vacancies in the ZnO lattice. Therefore, for the film produced at 780 °C, the intensity ratio of UV/deep-level emissions becomes very small (Fig. 4, curve 4). This also suggests that green emission is related to oxygen vacancies in the ZnO. The orange emission for nanorods fabricated at low temperature (550 °C), though not being fully understood, possibly results from the interstitial oxygen ions due to a relatively low temperature.[22] Orange PL has been seen in ZnO grown electrochemically, hydrothermally, and by PLD and spray pyrolysis.[23]

The PL spectra of ZnO nanorods deposited at 10 Torr pressure on a silicon substrate seem different from those for nanorods on a sapphire substrate, as shown in Fig. 5. The extremely strong UV emissions and negligible deep-level emissions imply that the nanorods obtained on a Si substrate have a better structural quality. The reason may be explained by the interface stress based on different substrates. The details, however, need to be further intestigated. Sans *et al.*[24] investigated PL properties of ZnO films prepared on sapphire, fluorite and mica substrates, and found that the nature of the substrate greatly affected the relative intensity of the PL lines. Except the emission intensity, a shift was also found in the UV peak for the nanorods on different substrates. For example, the nanorod array on sapphire substrate at 700 °C and 10 Torr has a band-edge UV emission at 386 nm, compared to 380 nm for that on silicon substrate at 600 °C and 10 Torr, though both of them have a similar rod size. The reason is possibly due to the different stress on these two substrates. The compression stress resulting from thermal expansion strain led to a shift in the band-edge maximum PL intensity.[25]

In conclusion, crystallized and *c*-axis oriented ZnO nanorods with various mean diameters have been grown on both sapphire and silicon substrates heated to 550 °C–700 °C at the background pressure of 5–20 Torr by a PLD technique without any catalyst. The PL properties for the nanorods with various sizes produced at various temperatures, pressures, and on different substrates have been explained by the structural defects, surface status, and structural stress.

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