Cathodoluminescence Properties of ZnO Tower-Like Structures Prepared by Thermal Oxidation*

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ZnO tower-like structures with hexagonal cross section were fabricated by a thermal oxidation method. Spatially resolved cathodoluminescence (CL) intensity images were employed to correlate the luminescent properties with the investigated structure. Local CL monochromatic images revealed that the bodies of ZnO tower-like structures were the major source for a strong green emission. The depth-resolved UV and green CL emissions were examined by changing the accelerating voltage. A part of reabsorbed UV emission is converted into green emission and partly contributes the enhancement of green emission. [DOI: 10.1380/ejssnt.2009.358]

Keywords: ZnO tower-like structures; Cathodoluminescence; Surface defect; Penetration depth

I. INTRODUCTION

As a representative semiconductor, ZnO has been intensively investigated from the interest and demand in the development of optoelectronic devices in an ultraviolet (UV) region and a visible region. Due to their unique semiconducting, piezoelectric properties, as well as biosafety and biocompatibility, nanostructured ZnO materials have also attracted much interest in recent years [1–3]. Possessing a wurtzite lattice structure of non-central symmetry and a combination of the preferential growth along the (0001) direction, ZnO can manifest itself in a wide range of diverse one-dimensional (1D) structures under appropriate conditions. The 1D structure can provide a direct path carriers transport and it makes 1D ZnO being one of the ideal materials for the study of quantum confinement effects and nanodevice physics. Accordingly, extensive research has been focused on 1D ZnO structures including wires, rods and tubes, which are prepared by traditional approaches such as vapor phase transport [4] and wet chemical method [5]. Some defects such as dislocations, point defects and stacking faults can be observed in the structures, and they affect the optical properties of 1D ZnO significantly [6]. A large number of reports pay more attention on photoluminescence (PL) properties of 1D ZnO structures [7–10]. However, for most of these studies, the spatial resolution for the PL is about micrometer range. It leads to average over a few nanostructures with typical diameters in the range of 100 nm. In order to get the detailed emission information from tiny area, even from individual nanostructures, to clarify the origin of specific emission, a probe with high spatial and spectral resolutions is preferable. Compared with PL, CL can potentially give additional information on a local position in the sample, since electron beam can be focused on several nanometers. On the other hand, the depth dependent emission profiles can be examined through the control of the accelerating voltage [11–13].

Although CL has been widely used for the material characterizations, systematic CL investigation on 1D ZnO is still limited. In this article, we have fabricated 1D ZnO tower-like structure by the thermal oxidation process. Spatially and spectrally resolved CL microscopy was employed in order to correlate the local optical with the structural properties of ZnO towers. The depth resolved CL was also examined. The variations of the near band edge emission are affected by the self-reabsorption, which leads to the increasing visible emission intensity with depth.

II. EXPERIMENT

The ZnO tower-like structures were fabricated by the thermal oxidation process in diffusion and premixed flames, by seeding the fuel with galvanized steel without catalysts [14]. The burner was a commercially available...
III. RESULTS AND DISCUSSION

Figure 1 shows scanning electron microscope (SEM) images of the as-grown ZnO. It is clearly illustrated that the resulting sample is like a tower with various directions. At the bottom, several individual tower-like structures are jointed together. Each ZnO tower has a regular hexagon cross section (HCE) with uneven lateral length of HCE along its entire length from 500 nm at top to 2 \( \mu m \) at bottom. A representative EDX spectrum (Fig. 1(b)) reveals that all towers-like structures are composed of only Zn and O, and no other metal element is found. The formation of ZnO structures can be enucleated by the vapor-solid mechanism. Under high temperature, Zn from the surface layer is evaporated and oxidized by the oxygen in the air. The ZnO nucleuses are formed from the supersaturation of zinc vapor. The tower-like growth pattern may originate from the fast growth rate along (0001) direction, which makes Ostwald ripening only affect the ZnO crystal morphology slightly and the kinetic confinement results in the presence of steps on the side surface of ZnO [16].

Figure 2(a) illustrates the CL spectra recorded at the beam accelerating voltage of 10 kV. It is found that the profile shows the typical ZnO spectra shape, composing of the UV emission peak and the visible emission band centered at green wavelength about 530 nm. The UV peak is known due to the transition from the conduction band to the valence band [17]. However, the origin of green emission is still controversial and several mechanisms have been proposed, such as intrinsic defect origin or extrinsic impurity (Cu ion) induced. Whatever, a green emission in ZnO is believed to be associated with defects and impurities. In our case, no extrinsic impurity existed in the samples from the result of EDX. Therefore, it is expected that defects both in volume and in surface contribute the green emission. It has been reported that a narrow green emission band is due to oxygen vacancy [18]. However, the full width at half maximum (FWHM) of the green band in all investigated structures is about 400 meV. This fact indicates that several kinds of defects being associated with the native point defects (such as oxygen or zinc vacancy, interstitial oxygen or zinc), the defects due to surface absorption or arising directly from the atomic structure of the dislocations may contribute to this broad green band.

Correspondingly, the spatial distribution of UV and green band emissions is given by the CL intensity images, as shown in Figs. 2(b) and 2(c), respectively. It can be thought of as a map of the efficiency of luminescence excited by the scanned electron beam at the selected emission wavelength. Compared with the SEM image of the same area (the inset of Fig. 1(a)) with each CL image, it can be directly seen where the origin of the luminescence peaks are. Here, the bright (dark) spots in the CL image represent high (low) CL emission intensity. It is clearly illustrated in Fig. 2 that the body of tower-like structure mainly contributes the green emission. It correlates...
well with the widely accepted fact that defects located at the surface are mainly responsible for green emission in ZnO structures. The UV emission, on the other hand, is observed from the bottom junctions of the tower-like structure. These observations show that the nonuniform distribution of the CL intensity is observed across the investigated structure.

In order to further understand the emission property from ZnO tower-like structures, it is necessary to clarify the effect of electron beam conditions on CL measurement. Accelerating voltage is considered as a main parameter affecting electron beam [19]. Therefore, the depth dependent CL spectra on the beam accelerating voltage were investigated, as displayed in Fig. 3. Figure 3 also exhibits the integrated UV and green band emissions as a function of the accelerating voltage. The number of excited carriers is considered to be in proportion to accelerating voltage, since the CL intensity in the ZnO tower-like structures increases linearly with accelerating voltage (Fig. 3). In order to emphasize the influence of changing the excitation volume on the CL efficiency, therefore, both emission intensities are divided by the product of accelerating voltage and beam current. The UV intensities linearly increase to 14 kV and tend to saturation afterwards, while green band emission shows continuous increasing with the accelerating voltage. With the accelerating voltage increasing, higher electron beam is expected to penetrate deeper structures and excites others near and below them. In this way, more emission centers will be excited by the electron bombardment. However, it’s not

all the UV emissions contribute to the CL signal. It is found in ZnO bulk and thin films that the UV emission from ZnO can be internally reabsorbed by the crystal itself within in 1 µm [20]. Consequently, the CL efficiency in UV region stops increasing when the accelerating voltage over 14 kV (corresponding to the penetration depth about 1 µm), but shows the saturating tend. However, this reabsorbed UV emission can excite defect states in the structures and gives back the green emission. Thus, a part of UV emission may be converted into green emission and contributes the enhancement of green emission.

IV. SUMMARY

We have grown the 1D ZnO tower-like structures by an easy, inexpensive thermal oxidation method. Optical emission property was detailed studied by employing CL method. A strong green emission from the nanotowers was observed because of larger number of surface defect. The emission intensity was affected by the penetration depth of electron beam. It is considered that the green emission increases with increasing the accelerating voltage due to the conversion of self-absorbed UV emission.
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