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Determination of the microstructure of Eu-treated ZnO nanowires by x-ray absorption

W. L. Huang,1 J. Labis,1,a) S. C. Ray,1,2 Y. R. Liang,1 C. W. Pao,1 H. M. Tsai,1 C. H. Du,1 W. F. Pong,1(b) J. W. Chiou,3 M.-H. Tsai,4 H. J. Lin,5 J. F. Lee,5 Y. T. Chou,6 J. L. Shen,6 C. W. Chen,7 and G. C. Chi8

1Department of Physics, Tamkang University, Tamsui 251, Taiwan
2School of Physics, University of the Witwatersrand, Private Bag 3, WITS 2050, Johannesburg, South Africa
3Department of Applied Physics, National University of Kaohsiung, Kaohsiung 811, Taiwan
4Department of Physics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan
5National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan
6Department of Physics, Chung Yuan Christian University, Chungli 320, Taiwan
7Department of Physics, National Central University, Chungli 320, Taiwan
8Department of Photonics, National Chiao Tung University, Hsinchu 300, Taiwan

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X-ray absorption near-edge structure (XANES), extended x-ray absorption fine structures (EXAFS), and photoluminescence measurements were used to elucidate the microstructural and photoluminescence properties of ZnO nanowires (ZnO-NWs) that had been treated with Eu by thermal diffusion. The O K- and Eu L3-edge XANES and EXAFS spectra at the Zn K- and Eu L3-edge verified the formation of Eu2O3-like layer on the surface of ZnO-NWs. X-ray diffraction, XANES and EXAFS measurements consistently suggest the lack of substitutional doping of Eu ions at the Zn ion sites in the interior of ZnO-NWs. The clear sharp and intense emission bands in the range 610–630 nm of Eu-treated ZnO-NWs originated from the intra-4f transition of Eu ions in the Eu2O3-like surface layer. © 2010 American Institute of Physics. [doi:10.1063/1.3304071]

Zinc oxide (ZnO) is a well-known wide band-gap semiconductor with a large exciton binding energy at room temperature. It has attracted much interest in recent years because of its unique properties and potential applications.1–4 Recent studies of this material have focused on its applications in optoelectronics and light-emitting devices. ZnO emits over a wide range of the visible spectrum and UV luminescence. Many studies of rare-earth (RE)-treated ZnO and RE-induced changes in their optical properties have tended to conclude that trivalent RE ions are effective luminescence centers.4–7 The results of these studies have also suggested that energy can be transferred from the ZnO matrix to Eu activator ions, yielding narrow and intense emission lines that are associated with 4f intrashell transitions. However, the direct transfer of energy from ZnO to Eu ions has been argued to be unfeasible, because the lifetime of the exciton in ZnO is much shorter than the time required for energy transfer,8 the difference between ionic radii exceeds that of Zn2+ (0.74 Å), such that the substitution increases the interplane distance. However, the XRD data in Fig. 1 do not reveal any diffraction peak shift, seemingly excluding the possibility of substitutional doping by Eu ions at the Zn ion sites in the interior of Eu-treated ZnO-NWs. The high-resolution transmission electron microscopy (HR-TEM) image in inset (a) in Fig. 1 reveals sharp and clear ordered-lattices in ZnO-NWs.

a)Also at permanent address: Department of Physics, College of Science, MSU-General Santos City, Philippines.

b)Author to whom correspondence should be addressed. Electronic mail: wfpong@mail.tku.edu.tw.
In contrast, the HR-TEM image in inset (b) displays relatively oblique and disoriented-lattices in Eu-treated ZnO-NWs, attributable to the presence of Eu-oxide on the surface. The scanning electron microscopic (SEM) image in inset (c) shows the round structure of Eu-treated ZnO-NWs and their overall growth in the upright/vertical direction associated with the thermal diffusion of Eu atoms. Panels [(d)–(f)] in Fig. 1 present the PL spectra of Eu-treated ZnO-NWs under excitation by 260 (4.77 eV), 396 (3.13 eV), and 470 (2.64 eV) nm He-Ar laser light at 15 K. The figure reveals strong near-band-edge emission at ~370 nm (3.3 eV). Corresponding green luminescence is centered at ~500 nm [panel (d)] and sharp and intense emissions are observed in the spectra in the range 610–630 nm [panels (d)–(f)] under the three excitations. The broad green luminescence in panel (d) has been suggested to be caused by vacancy defects. The shift in the broad green luminescence of Eu-treated ZnO-NWs relative to that of ZnO-NWs is attributable to deep trapped hole states in oxygen vacancies and excess oxygen on the surface of NWs. Panels (d)–(f) also present the PL spectra of ZnO-NWs and Eu$_2$O$_3$ under various excitations at 15 K for comparison. Clearly, the excitation energies at 396 (3.13 eV) and 470 nm (2.64 eV) are lower than the band gap of pure ZnO-NWs (~3.4 eV). The sharp and intense emissions in the range 610–630 nm from Eu-treated ZnO-NWs under various excitations suggest that Eu ions may gain energy from ZnO-NWs, giving rise to an intra-4$f$ transition. The emissions in the range 610–630 nm of Eu-treated ZnO-NWs are similar to those of the reference Eu$_2$O$_3$, as shown in panels (e) and (f) in Fig. 1. Careful observation reveals that, in spite of discernible similarity, the Stark splitting in the spectra are still somewhat different, which can be explained by the highly defective nature of the produced Eu$_2$O$_3$-like layer that covers the surface. The formation of other compounds, such as ZnEu$_2$O$_4$, which has been reported to be a stable oxide, could also be a possibility, although the analysis of the data in the present work shows that the Eu$_2$O$_3$-like layer is most likely.

Figure 2 presents normalized O K-edge XANES spectra of Eu-treated, untreated ZnO-NWs, and reference Eu$_2$O$_3$. The characteristic features A$_1$–E$_1$ in the O K-edge spectrum of ZnO-NWs corresponds primarily to O $1s$ transitions to O $2p_{3/2}$, O $2p_{1/2}$, and O $2p_{3/2}$. Corresponding green luminescence is centered at ~500 nm [panel (d)] and sharp and intense emissions are observed in the spectra in the range 610–630 nm [panels (d)–(f)] under the three excitations. The broad green luminescence in panel (d) has been suggested to be caused by vacancy defects. The shift in the broad green luminescence of Eu-treated ZnO-NWs relative to that of ZnO-NWs is attributable to deep trapped hole states in oxygen vacancies and excess oxygen on the surface of NWs. Panels (d)–(f) also present the PL spectra of ZnO-NWs and Eu$_2$O$_3$ under various excitations at 15 K for comparison. Clearly, the excitation energies at 396 (3.13 eV) and 470 nm (2.64 eV) are lower than the band gap of pure ZnO-NWs (~3.4 eV). The sharp and intense emissions in the range 610–630 nm from Eu-treated ZnO-NWs under various excitations suggest that Eu ions may gain energy from ZnO-NWs, giving rise to an intra-4$f$ transition. The emissions in the range 610–630 nm of Eu-treated ZnO-NWs are similar to those of the reference Eu$_2$O$_3$, as shown in panels (e) and (f) in Fig. 1. Careful observation reveals that, in spite of discernible similarity, the Stark splitting in the spectra are still somewhat different, which can be explained by the highly defective nature of the produced Eu$_2$O$_3$-like layer that covers the surface. The formation of other compounds, such as ZnEu$_2$O$_4$, which has been reported to be a stable oxide, could also be a possibility, although the analysis of the data in the present work shows that the Eu$_2$O$_3$-like layer is most likely.

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FIG. 3. (Color online) FT of EXAFS $k^2\chi$ data from $k=3.2$ to 13.5 Å at Zn $K$-edge of Eu-treated ZnO-NWs, and ZnO-NWs, and Eu $L_1$-edge from $k=3.2$ to 10.5 Å of Eu-treated ZnO-NWs and Eu$_2$O$_3$ powder, respectively. Upper left part of inset presents experimental geometry, where $E$ is the polynomial of the incoming photons, and $\theta$(=37°) is the angle of incidence. Upper right inset presents the Zn $K$-edge EXAFS $k^2\chi$ data of Eu-treated ZnO-NWs and ZnO-NWs. Lower right inset shows Eu $L_1$-edge EXAFS $k^2\chi$ data of Eu-treated ZnO-NWs and Eu$_2$O$_3$.

(NN) Zn–O and the next-nearest-neighbor (NNN) Zn–Zn bond lengths. Clearly, the line-shapes and the radial distribution of the FT spectra at the Zn $K$-edge of the Eu-treated ZnO-NWs are nearly identical to those of ZnO-NWs but the overall spectral intensities of the NN and NNN features are slightly higher. These results suggest the following. (i) Eu atoms in the thermal diffusion process did not substitute for host Zn ions in Eu-treated ZnO-NWs, because if the Eu atoms had randomly substituted Zn ions in the interior of the NWs, the local atomic structure at the Zn sites should be strongly distorted, due to the large difference between the ionic radii of Eu$^{3+}$ and Zn$^{2+}$, and such distortion was not observed. The XRD data are consistent with this finding. (ii) Most of the Eu atoms substituted at the Zn sites on the surface layer and formed a stable Eu$_2$O$_3$-like layer, such that Zn ions with dangling bonds or defects, which have a larger degree of disorder, were depleted. This argument explains why the spectral intensities of the NN and NNN features in the FT spectra of Eu-treated ZnO-NWs slightly exceed those of Eu$_2$O$_3$. Clearly, the line-shapes and the radial distribution of the Eu $L_1$-edge FT spectra of Eu-treated ZnO-NWs are similar to those of reference Eu$_2$O$_3$, indicating that the local atomic structure of Eu ions in Eu-treated ZnO-NWs is similar to that of Eu$_2$O$_3$. The lower intensities of the NN and NNN features in the FT spectra of the Eu-treated ZnO-NWs reveal that the structural distortion of Eu-treated ZnO-NWs exceeds that of Eu$_2$O$_3$, possibly because of an increase in the number of dangling bonds/surface states of the Eu$_2$O$_3$-like layer on the surface of ZnO-NWs.10,11 Notably, the EXAFS FT spectra of the Eu $L_1$-edge of the Eu-treated ZnO-NWs clearly differ from those at the Zn $K$-edge, further indicating the lack of significant substitution of Zn ions by Eu ions in Eu-treated ZnO-NWs. Additionally, polarization-dependent EXAFS measurements (not shown in the figure) at the Eu $L_3$-edge, with two angles of incidence, $\theta=0°$ (normal incidence) and $70°$ (grazing incidence), were also made. The spectral intensities of the NN and NNN features in the FT spectra at $\theta=70°$ are lower than those at $\theta=0°$, suggesting greater surface sensitivity at the grazing incidence, which is associated with larger structural disorder, and leads to the detection of more dangling bonds or defects on the Eu$_2$O$_3$-like surface layer. This finding is evidence of the presence of an Eu$_2$O$_3$-like surface layer. If Eu ions had been incorporated at the interstitial sites of the grain boundaries in the ZnO-NWs matrix, polarization-dependent EXAFS measurements would differ negligibly between the two incident angles.

As stated above, the enhancement of PL in Eu-treated ZnO-NWs is generally believed to involve the absorption of photon energy by Eu ions, causing their electrons to transition from the ground state to the excited state. This process may be associated with structural defects, chemical inhomogeneities, and oxygen vacancies formed by Eu. When ZnO-NWs absorb photon energy, electron-hole pairs are generated. Some of the energy that is released by the recombination of electron-hole pairs is transferred to Eu ions, so that they act as luminescence centers with $4f$ intrashell transitions, yielding narrow and intense emission lines under indirect excitation.4,7 However, earlier studies have also shown that the transfer of energy from the ZnO host to Eu ions is very inefficient in Eu-treated ZnO.8,9 The measurements in this work demonstrate that the sharp and intense emission formed by Eu-treated ZnO-NWs originates at the Eu centers in the Eu$_2$O$_3$-like surface layer under direct light excitation.

18Table of Periodic Properties of the Elements (Sargent-Welch Scientific, Skokie, IL, 1980).