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Size-dependent surface luminescence in ZnO nanowires

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Nanometer sized whiskers (nanowires) offer a vehicle for the study of size-dependent phenomena. While quantum-size effects are commonly expected and easily predicted, size reduction also causes more atoms to be closer to the surface. Here we show that intensity relations of below-band-gap and band-edge luminescence in ZnO nanowires depend on the wire radius. Assuming a surface layer wherein the surface-recombination probability is 1 (*surface-recombination approximation*), we explain this size effect in terms of bulk-related to surface-related material-volume ratio that varies almost linearly with the radius. This relation supports a surface-recombination origin for the deep-level luminescence we observe. The weight of this surface-luminescence increases as the wire radius decreases at the expense of the band-edge emission. Using this model, we obtain a radius of 30 nm, below which in our wires surface-recombination prevails. More generally, our results suggest that in quantum-size nanowires, surface-recombination may entirely *quench* band-to-band recombination, presenting an efficient sink for charge carriers that unless deactivated may be detrimental for electronic devices.

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I. INTRODUCTION

Nanowire research was originally propelled by the quest for a quasi-one-dimensional quantum structure for laser diode applications.[1–3] Later, it was shown that semiconductor whiskers could be grown at the nanometer scale,[4] and this method has gradually been recognized as a means to achieve control over material structure for a variety of nanometer-scale applications.[5,6] While the whisker growth mechanisms have been long established,[7,8] unexpected material properties are often encountered at the nanometer scale.[9,10] Comparing photoluminescence spectra of bulk ZnO wafer and ZnO nanowires, one encounters a profound difference in the form of a wide below-band-gap emission band, characteristic of the wire-structured ZnO (Fig. 1). *Prima facie*, this wide parasitic light emission suggests these nanowires are fairly rich in defects. Conversely, nanowires are often claimed to be rather devoid of defects. What then is the source of this peculiar below-band-gap luminescence in nanowires?

One of the first peculiar properties observed in whiskers was their tensile strength.[11] Already in 1956, Brenner showed that the strength of whiskers increases as their diameter is made smaller. He attributed this behavior to a reduction in the number of defects with size.[12,13] Possibly, as the diameter decreases, the surface approaches the bulk, providing a natural energy sink, where defects and impurities can segregate. This mechanism may leave the bulk with a relatively small concentration of defects as compared to the surface, while the surface, a crystalline imperfection by definition, receives defects and contaminations segregating from the bulk during the growth as well as contaminations adsorbed onto it after the growth. It is also intuitively clear that localized-defect-induced strain is likely to be at least partially relieved by bending or kinking a nanowire, while bulk material is less likely to allow this type of strain relief. Indeed, transmission electron microscopy studies have shown that bent and curved nanowires contained localized defects at the bending regions, whereas straight nanowires were generally devoid of them.[14,15] This facilitates an easy-to-use selection criterion. While defects may still exist in straight wires, they should be more likely limited to surfaces and interfaces. We therefore limit our discussion to nanowires that appear to have a straight morphology.

This study was undertaken to examine the parasitic visible luminescence band in straight ZnO nanowires. The hypothesis tested was that this deep-level luminescence originates at surface states, i.e., special electronic states characteristic of the material surface. If the surface is the origin, then *reduction* of the crystallite size should be expected to *increase* the relative intensity of this emission. This is because the weight of the surface-related volume, i.e., a volume of a thin surface layer hosting the surface states, increases relative to the weight of bulk-related volume, thereby increasing below-band-gap emission at the expense of the band-edge emission.

II. MODEL

Quantitatively, let us consider a wire of length l, radius r, where $l \gg r$. Although surface states can be associated only with the very few top monolayers of the material, the effective volume that contributes to surface recombination includes a certain effective diffusion length, i.e., a distance, t, within which carriers can diffuse to the surface before they recombine. In practice, the probability for surface recombination drops gradually with the depth of the excited carrier. Our *surface-recombination-layer approximation* assumes a layer of thickness t, wherein the probability for surface recombination is 1. The volume associated with the wire surface, V_S, is then

$$V_S = l\pi[r^2-(r-t)^2]. \tag{1}$$

The remaining volume of the wire, V_B, associated with the bulk, is then

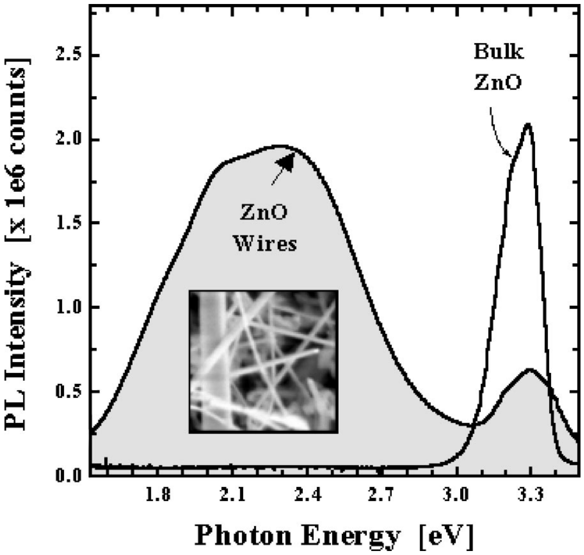

FIG. 1. Photoluminescence spectra obtained from a bulk single crystal of ZnO and from ZnO nanowires grown on a Si(111) substrate. The nanowire radii in this sample varied broadly between 30 and 250 nm.

$$V_B = l\pi(r-t)^2. \tag{2}$$

The ratio between these volumes is

$$\frac{V_B}{V_S} = \frac{r^2}{2rt-t^2} - 1. \tag{3}$$

As r approaches the order of l, the term $2rt$, in the denominator, gradually changes to $3rt$, as in the case of spherical dots.

Equation (3) shows that the volume ratio between bulk wire material and material associated with the wire surface is nearly *linear* with the wire radius. If this volume ratio is a dominant factor, we can predict that the ratio between band-edge and below-band-gap luminescence peak intensities, $I_{\mathrm{BE}}/I_{\mathrm{BG}}$, will vary with the wire radius to reflect the changes in the relative weights of bulk and surface volumes. That is

$$\frac{I_{\mathrm{BE}}}{I_{\mathrm{BG}}} = \frac{H(\lambda_{\mathrm{BE}})}{H(\lambda_{\mathrm{BG}})}\,\frac{\eta_{\mathrm{BE}}}{\eta_{\mathrm{BG}}}\,\frac{V_B}{V_S} = C\,\frac{V_B}{V_S}, \tag{4}$$

where I_{BE} and I_{BG} and η_{BE} and η_{BG} are the peak intensities and processes efficiencies of band-edge and below-band-gap emissions, respectively. $H(\lambda)$ is the transmission of the optical system at a wavelength λ. For our system $H(375\ \mathrm{nm})/H(555\ \mathrm{nm}) \approx 0.8$. Substituting Eq. (3) into (4), we get

$$\frac{I_{\mathrm{BE}}}{I_{\mathrm{BG}}} = C\left(\frac{r^2}{2rt-t^2} - 1\right). \tag{5}$$

Equation (5) provides for our main prediction: If the process efficiencies do not depend on the radius, the relative intensities of the band-edge and below-gap emission peaks should vary almost linearly with the wire radius. The band-edge emission may still have another dependence on the radius through the *absorption coefficient*. However, this effect is likely to be felt only in thick wires.

Fragmentary evidence for the behavior described in our model, observed in quantum dots and nanowires, clearly supports the proposed trend.[16,17] However, the large variability of surface state densities makes it difficult to obtain meaningful results when the experimental variables are not precisely controlled. We now test this model experimentally on ZnO nanowires.

III. EXPERIMENTAL DETAILS

We grew the ZnO nanowires by chemical vapor deposition on Si(111) wafers. As a source, we used a mixture of ZnO and graphite powders held at 1030 °C, while the substrate was held at a region where the temperature gradient ranges from 930 to 990 °C in a flow of 30 SCCM of Ar for 30 min. The ZnO wafer used as reference was purchased from Cermet Inc. Photoluminescence (PL) was excited at room temperature using a HeCd laser (325 nm, 8 mW). The emitted luminescence was monochromatized, filtered, and sensed using a Si charge coupled device camera. To eliminate hidden variables as much as possible, all the various thickness wires were grown in the same run, and all the spectra were obtained in one session under identical excitation and collection conditions. Scanning electron microscopy was carried out in a LEO-A (Zeiss) 982 FEG-SEM (field emission gun scanning electron microscope) at 2 kV at a distance of 4 mm. Examination of selected nanowires by transmission electron microscopy confirmed their crystallinity.

IV. RESULTS AND DISCUSSION

Figure 2 shows three photoluminescence spectra with SEM images of the crystalline structure at the related spots. Two main features are observed. A band-edge peak at about 3.3 eV, and a below-band-gap peak centered at about 2.2 eV. The relative strength of the band-edge photoluminescence peak, compared with the deep level luminescence, is seen to change with the size of the wires. The first set of wires (left panel), with diameters around 100 nm, shows a weak band-edge emission. Its PL is dominated by emission from deep levels but the band-edge related peak remains visible. Larger wires with diameters of ~240 nm (center panel) show room temperature PL with a significantly stronger band-edge emission. In wires with diameters of ~540 nm, shown on the right panel, the band-edge PL is quite strong and the below-band-gap luminescence becomes relatively weak.

Figure 3 presents the luminescence peak intensity ratios obtained from the curves of Fig. 2 and two additional spectra (all spectra shown in the inset) as a function of the average wire radius. The error bars stand for the standard deviations of the radii. Fitting the data with Eq. (5) yields $C = 2.3$, which means the efficiency of the bulk-related emission process exceeds that related to the surface by factor of 2.9. The other fit parameter, the depth of the surface-recombination-layer, t, is found to be 30 nm. It represents an *effective* dis-

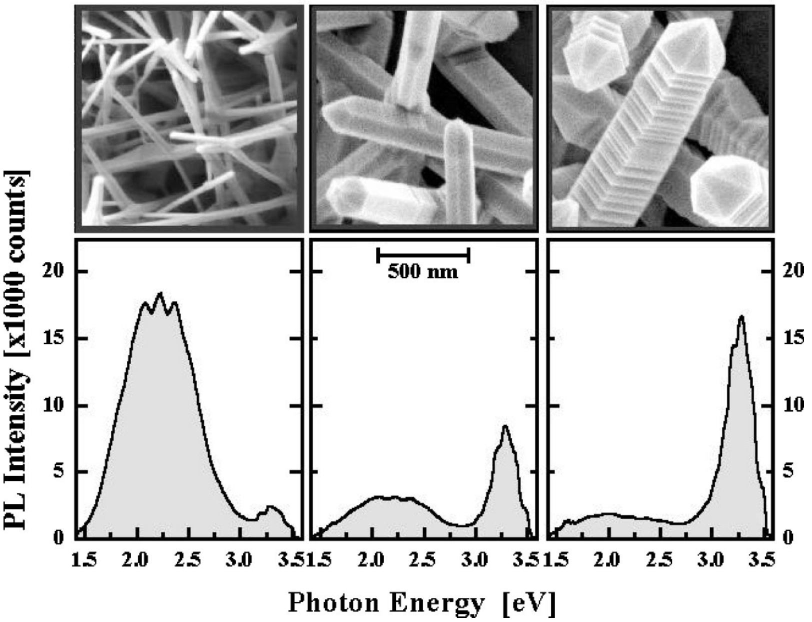

FIG. 2. Photoluminescence spectra obtained from ZnO wires of three different sizes. Scanning electron microscope images of the typical crystalline structures at each of the spots are shown above each of the spectra.

tance from the surface, within which the excited carriers recombine at the surface. Surprisingly, this depth exceeds the radius of most of the quantum-size nanowires. This value has an important implication: Below a certain size, the luminescence properties of our ZnO nanowires should be *entirely* dominated by properties of the surface. According to Eq. (5) the band-edge luminescence peak should be nullified for $r = t$, while for $r < t$ our surface-recombination-layer approximation breaks. In practice, however, there is a tail of exponentially diminishing probability at $r < t$. Clearly, for $r \approx t$, most of the carriers excited throughout the volume can diffuse to the surface, and henceforth, *surface recombination prevails*. This is true as long as the pumping rate does not exceed the surface-recombination rate, i.e., a high enough pumping rate may still produce band-to-band recombination because the surface states are only capable of recombining a limited number of carriers at a given time.

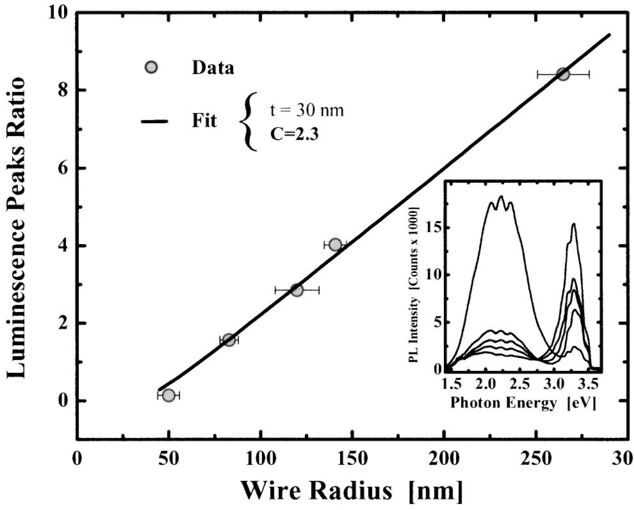

FIG. 3. Luminescence peak intensity ratios as a function of the average wire radii, and a fit using Eq. (5).

Figure 3 provides a quantitative confirmation of the prediction made in Eq. (5) and therefore corroborates the model given. This result suggests that surface states decorating the surface of our ZnO wires emit visible luminescence, with efficiency that increases as the wire dimension diminishes, while quenching band-edge emission. This result is independent of the specific chemical identity of the trap or its physical properties, which have been studied in the past but remain to be fully understood.[18,19]

We wish to emphasize that the value of 30 nm we obtain for the surface-recombination layer thickness is by no means a general characteristic of ZnO. Surface-state densities are infamous for their great variability. They can vary from one growth run to another and can sometimes also vary with time. However, our results indicate that surface recombination can, under certain conditions, entirely eclipse band-to-band recombination in nanowires, and low-dimensional structures alike.

The implications of these results may not be limited to ZnO. For example, CdS, ZnS, and GaN nanostructures, whiskers, and films often show a wide below-gap luminescence band.[20–24] Very recently, polymer capping of ZnO and CdS quantum dots was shown to efficiently minimize this deep-level emission.[25,26] Reynolds *et al.* show that the *yellow luminescence* band in GaN is similar in various characteristics to the green luminescence band in ZnO.[27] This yellow luminescence is also common in GaN films, probably because a monocrystalline form of GaN is still uncommon. Ponce and Bour showed with cathodoluminescence that the yellow luminescence is emitted mainly from the GaN grain boundaries.[28] The nature of the yellow luminescence band in GaN has been extensively studied, and has recently been suggested to originate at surface states.[29–31] In spite of the extensive work, the source of the yellow luminescence in GaN is a subject of much debate as several studies have suggested a bulk state.[32] The method suggested in this study may prove useful in resolving this controversy.

The effect of surface recombination may not be limited to quenching of band-to-band recombination, but may actually provide an undesirable trap for excess carriers in other device applications. It may therefore have a crucial weight in various device applications of quantum-size nanowires, and may require solutions such as heterostructure cladding. Alternatively, this sensitivity to surface properties may find use in sensor applications. The concept of surface-recombination layer approximation presented here may find use as a theoretical as well as experimental handle in studying the effect of surface states on low dimensional structures.

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[1] P. M. Petroff, A. C. Gossard, and W. Wiegmann, Appl. Phys. Lett. **45**, 620 (1984).

[2] D. Gershoni, H. Temkin, D. J. Dolan, J. Dunsmuir, S. N. G. Chu, and M. B. Panish, Appl. Phys. Lett. **53**, 995 (1988).

[3] P. L. Gourley, Nature (London) **371**, 571 (1994).

[4] M. Yazawa, M. Koguchi, and K. Hiruma, Appl. Phys. Lett. **58**, 1080 (1991).

[5] C. M. Lieber, Sci. Am. **285** (3), 58 (2001).

[6] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science **292**, 1897 (2001).

[7] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).

[8] E. I. Givargizov, J. Cryst. Growth **31**, 20 (1975).

[9] R. N. Barnett and U. Landman, Nature (London) **387**, 788 (1997).

[10] M. S. Dresselhaus, Y.-M. Lin, O. Rabin, A. Jorio, A. G. S. Filho, M. A. Pimenta, R. Saito, G. G. Samsonidze, and G. Dresselhaus, Mater. Sci. Eng., C **23**, 129 (2003).

[11] W. C. Herring and J. K. Galt, Phys. Rev. **85**, 1060 (1952).

[12] S. S. Brenner, J. Appl. Phys. **27**, 1484 (1956).

[13] S. S. Brenner, Science **128**, 569 (1958).

[14] N. Wang, Y. H. Tang, Y. F. Zhang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, Chem. Phys. Lett. **283**, 368 (1998).

[15] Defects that extend along the wire (in the growth direction), around which whiskers sometimes develop, may still exist even in straight wires (see mechanism described in Ref. 2).

[16] A. van Dijken, J. Makkinge, and A. Meijerink, J. Lumin. **92**, 323 (2001).

[17] M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, Adv. Mater. (Weinheim, Ger.) **13**, 113 (2001).

[18] K. Vanheusden, W. L. Waren, C. H. Seager, D. R. Tallant, J. A. Voigt, and B. E. Gnade, J. Appl. Phys. **79**, 7983 (1996).

[19] H. Zhou, H. Alves, D. M. Hofmann, W. Kriegseis, B. K. Meyer, G. Kaczmarczyk, and A. Hoffmann, Appl. Phys. Lett. **80**, 210 (2002).

[20] M. O'Neil, J. Marohn, and G. McLendon, J. Phys. Chem. **94**, 4356 (1990).

[21] R. Takahashi, J. Lumin. **24-25**, 67 (1981).

[22] Y. Wang, L. Zhang, C. Liang, G. Wang, and X. Peng, Chem. Phys. Lett. **357**, 314 (2002).

[23] L. S. Marasina, I. G. Pichugin, Yu. M. Suleimanov, and S. I. Teslenko, Sov. Phys. Semicond. **8**, 1187 (1974).

[24] T. Ogino and M. Aoki, Jpn. J. Appl. Phys. **19**, 2395 (1980).

[25] L. Guo, S. Yang, C. Yang, P. Yu, J. Wang, W. Ge, and K. L. W. Wong, Appl. Phys. Lett. **76**, 2901 (2000).

[26] S. H. Liu, X. F. Qian, J. Yin, X. D. Ma, J. Y. Yuan, and Z. K. Zhu, J. Phys. Chem. Solids **64**, 455 (2003).

[27] D. C. Reynolds, D. C. Look, B. Jogai, and H. Morkoc, Solid State Commun. **101**, 643 (1997).

[28] F. A. Ponce and D. P. Bour, Nature (London) **386**, 351 (1997).

[29] I. Shalish, L. Kronik, G. Segal, Y. Shapira, S. Zamir, B. Meyler, and J. Salzman, Phys. Rev. B **61**, 15573 (2000).

[30] I. Shalish, C. E. M. de Oliveira, Y. Shapira, and J. Salzman, Phys. Rev. B **64**, 205313 (2001).

[31] I. Shalish, L. Kronik, G. Segal, Y. Shapira, M. Eizenberg, and J. Salzman, Appl. Phys. Lett. **77**, 987 (2000).

[32] See, for example, K. Saarinen, T. Laine, S. Kuisma, P. Nissilä, P. Hautojärvi, L. Dobrzynski, J. M. Baranowski, K. Pakula, R. Stepniewski, M. Wojdak, A. Wysmolek, T. Suski, M. Leszczynski, I. Grzegory, and S. Porowski, Phys. Rev. Lett. **79**, 3030 (1997).