A fast sonochemical approach for the synthesis of solution processable ZnO rods

Marco Palumbo,^{a)} S. J. Henley, T. Lutz, V. Stolojan, and S. R. P. Silva

Nano-Electronics Centre, Advanced Technology Institute, University of Surrey, Guildford, GU2 7XH, United Kingdom

(Received 9 January 2008; accepted 13 August 2008; published online 2 October 2008)

A solution based sonochemical synthesis method for ZnO rods is presented with a resulting growth rate in excess of 15 times faster than previously reported. Such material is solution processable and could be exploited in the fabrication of transparent conductors and/or large area electronics via inkjet printing methods or solution based self-assembly techniques. To understand the crystal structure and defects chemistry, the as-synthesized wurtzite crystal structures were compared and contrasted with rods grown by the more traditional and well characterized hydrothermal growth method. Fluorescence spectra were recorded and the emission characteristics correlated with the structural and conductive properties of the ZnO rods. In particular, the sonochemical crystals appear to have a higher degree of order with fewer defects. This study represents a first step toward the tailoring of the electronic properties of ZnO rods. In particular, we will concentrate on the influence that native defects have on electrical conduction and on photoluminescence. Furthermore, we show how the intensity of the ultrasonic power exploited in this synthesis has a direct influence on the crystal quality as revealed by a comparative study. An optimum value between 30% and 35% of the maximum amplitude of a 20 kHz ultrasonic probe was found to give the best conditions for the growth of crystals with fewer defects density, while at ca. 25% of the maximum amplitude we observed the higher intensities for the fluorescence spectra both in the ultraviolet and in the visible range. © 2008 American Institute of Physics. [DOI: 10.1063/1.2988295]

I. INTRODUCTION

ZnO structures and thin films have regained increasing popularity in recent years as a result of their wide range of optical, piezoelectric, and magnetic properties. The large bandgap of 3.37 eV and its large exciton binding energy of 60 meV make it a very promising candidate for lasing based on excitation recombination at room temperature.¹ Furthermore, ZnO nanostructures have found application as light emitting devices,² solar cells,³ UV photo sensors,⁴ piezoelectric nanogenerators,⁵ and gas sensors.⁶

The synthesis methods of ZnO are quite diverse including pulsed laser ablation,^{7,8} chemical vapor deposition (CVD), metal-organic CVD, electrodeposition, and hydrothermal solution growth.^{9,10} This paper proposes an inexpensive method to generate, on a large scale and at moderate temperature, ZnO thin films and nanostructures with controlled complexity. In a hydrothermal decomposition reaction, a 1:1 molar solution of zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and hexamethylenetetramine (HMTA), $(\text{CH}_2)_6\text{N}_4$ is placed in an oven at 90 °C for 6 h. Consequently, hydroxide ions are formed by decomposition of HMTA and they react with Zn^{2+} to form ZnO

Normally, ZnO rods have hexagonal polar facets,¹⁰ which are an important element for lasing applications of ZnO structures, as the polar facets at the extremities act as the mirrors of a Fabry–Pérot cavity, while a reduced lateral scattering is guaranteed by the high refractive index of the ZnO ($n = 2.45$), with the rod effectively acting as a waveguide.^{1,11} An imperfect 1:1 molar ratio of the starting solution may result in an acicular shape of the rods. Previously, ultrasonication of a zinc nitrate and HMTA solution has been shown to accelerate the synthesis.^{12,13} In this work, we prove that it is possible to enhance even further the growth rate of the ZnO rods by combining ultrasonication with the use of a thermal bath. Through ultrasounds, mechanical energy is transferred to a reacting medium. Part of this energy will produce heat while another will cause cavitation, i.e., the production of microbubbles in a liquid when a large negative pressure is applied.¹⁴ These microbubbles act as microreactor because of the local increase in temperature and pressure at the moment of their collapse. Of particular interest for the formation of ZnO structures is the production of oxygen gas and hydrogen peroxide during the sonolysis of water in an air atmosphere.^{13,14} This extra oxygen may also react with the zinc ions in solution to produce ZnO

where the symbol))) indicates sonication (note that in a sonochemical process Eq. (3) as well is driven by sonication).

^{a)}Electronic mail: m.palumbo@surrey.ac.uk., Tel.: +44 (0) 148368 6088.

II. EXPERIMENTAL

To obtain an accelerated growth of ZnO rods, the use of a thermal bath is essential. In most cases, we used a simple beaker full of de-ionized water at a temperature of 70 °C. A thin bodied sonotrode connected to a 750 W, 20 kHz ultrasonic processor was introduced inside the reacting solution, previously heated up to 70 °C and contained in a glass vial placed inside the thermal bath, and ultrasonic power applied with an amplitude value set varying between 20% and 40% of the maximum value. Thin bodied sonotrodes are very effective to generate a small but very intense cavitation zone, while larger sonotrodes will produce larger but less intense cavitation zones despite transmitting a bigger ultrasound power. The reacting solution consisted of a 1:1 molar mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{CH}_2)_6\text{N}_4$ prepared in a range of concentrations going from 10^{-2}M to 10^{-4}M . The recorded value of the energy transferred by the tip to the solution during the process varied between 350 and 5000 J, directly proportional to the set amplitude value. Typically, the temperature of the external bath would drop from 70 to 50/55 °C at the end of the process. We found the drop in temperature to have an inverse relation with the power transferred to the solution. The maximum value and the pulse settings were 5 s on and 5 s off. In the first five seconds, energy is transferred from the microtip to the solution, while in the following 5 s sequential growth of the zinc oxide takes place. The produced ZnO rods were then separated from excess reagents and secondary reaction products via ultracentrifugation. Rods were resuspended in ultrapure water or organic solvent via sonication and vigorous agitation. Dimensions and crystal structures were determined by scanning and transmission electron microscopy (SEM and TEM). Fluorescence spectra were recorded using a xenon lamp spectrophotometer.

III. RESULTS AND DISCUSSIONS

The growth of ZnO rods was found to be dependent on using a thermal bath, which was fundamental to accelerating the growth. When a cooling bath was used or when the temperature of the solution in the vials was left to drift, we could not observe the formation of ZnO rods even when the sample was ultrasonicated for over 1 h. No ZnO rods were formed when the thin bodied sonotrode was replaced by a larger ultrasound probe with the amplitude set at $A=70\%$ with no external heat source applied to the reacting bath. Figure 1(a) shows that ZnO rods are consistently formed by two subunits attached end-to-end. In particular, the rods shown in Fig. 1(a) were synthesized from a mixture 10^{-3}M of zinc nitrate and HMTA. As a reference, ZnO rods grown using the hydrothermal method starting from a 10^{-3}M solution are shown in Fig. 1(b). The acicular shape is thought to derive from an imperfect 1:1 stoichiometry. From the analysis of similar SEM images, we observe that these rods come in two slightly different variations: the first one has two identical subunits with the same width and length, while for the second variant the two subunits have different widths but maintain consistent length. This observation on the length of the subunits appears to indicate that the growth process starts from a seed at the

FIG. 1. (a) SEM images of the result of ultrasound treatment of a 10^{-3}M zinc nitrate and hexamethylenetetramine solution. In the inset in the bottom-left corner, a detail of a flat hexagonal rod end is shown. (b) Hydrothermally synthesized ZnO rods.

center of the rods and then proceeds at constant speed in opposite directions along the same axis. Assuming a total rod length of $1.3\text{ }\mu\text{m}$ as for the rods in Fig. 1(a), the growth rate is 7800 nm h^{-1} , over 15 times faster than previously reported growth rates for sonochemical synthesis.¹³ Theoretically, our method could also be exploited for the growth of ZnO wires, provided that a steady flow of reagents is supplied to the reaction zone. This is at present the object of ongoing experimentation. A close examination of the ZnO rods reveals a hexagonal cross section as shown in the inset of Fig. 1(a), a feature relevant to lasing applications of structured ZnO films.^{1,11} The aspect ratio, length/width of the rods can be tuned by varying the molar concentration of the initial mixture. On average, from a 10^{-2}M solution rods with a width of ca. 400 nm and lengths of approximately $1\text{ }\mu\text{m}$ were obtained. It is worth stating that rods synthesized by a 10^{-2}M solution have a tendency to be thicker in the center and thinner at the extremities. Therefore, the value taken into account for the width was the average of the width measured halfway down the length of the two subunits. This particular phenomenon could be explained with the decrease in the free

FIG. 2. Crystallographic planes as revealed from high resolution TEM analysis. The distance between two adjacent planes indicated by arrows is 0.26 nm. In the inset (a), the corresponding electron diffraction pattern is shown.

zinc concentration during the growth process, which causes the variation in the ratio between the two-dimensional and the one-dimensional growth mode discussed in this paper.¹⁵ From a $10^{-3}M$ solution, we obtained ZnO rods with a width of approximately 200 nm and length of 1.3 μm , giving a resulting aspect ratio of 6.5. Slight variations in the growth parameters at times result in wider and longer rods (e.g., 500 nm wide and 3.5/4 μm long) with a consistent aspect ratio. This class of rods resulted in more uniform width values along their growth axis, in contrast with those prepared from the $10^{-2}M$ mixtures. Again, this seems to confirm that at low zinc concentrations, one-dimensional growth dominates over the two-dimensional growth mode.

To obtain the crystal structure of the ZnO rods produced, a few drops of a diluted dispersion in isopropanol were cast on a TEM grid coated with amorphous carbon. Due to rod thickness, lattice fringes were only visible at the very edges of the rods, as shown in Fig. 2. The high resolution TEM analysis indicates a wurzite crystallographic structure with the growth along the [0001] direction, the polar c -axis of the ZnO crystal lattice. The distance between the (0002) planes indicated by the arrows in Fig. 2 is of 0.26 nm, a value consistent with the wurzite crystal structure. The relative open structure of such a crystal with a hexagonal closed packed lattice, where the Zn atoms occupy half of the tetrahedral sites and where all the octahedral sites are empty, leaves plenty of sites to accommodate intrinsic defects and extrinsic dopants.⁹ This allows scope to fully exploit the properties of the ZnO structures by tuning its properties through doping (e.g., dilute magnetic semiconductor applications^{16–18}). The control of its defects chemistry and of the associated charge carriers would be ideally favored by such open structures.⁹

The luminescent properties of the ZnO rods at room temperature were investigated using a xenon lamp fluorescence spectrophotometer. A monochromator and filter were

FIG. 3. Fluorescence intensity vs emission wavelength for ZnO rods grown by the sonochemical method vs the fluorescence intensity of ZnO rods synthesized by hydrothermal decomposition.

used to isolate the excitation wavelength of 300 nm. Fluorescence spectra were recorded both for ZnO rods grown by the sonochemical method and for those grown by hydrothermal decomposition. In both cases the concentration of the initial reactants was $10^{-3}M$. To evaluate the effect of self-absorbance, we used a UV-Vis spectrometer scanning the response of the samples over a wavelength range going from 300 to 800 nm. At the concentrations investigated and for the purpose of our investigation, the UV-Vis response indicated a very negligible self-absorbent behavior (i.e., no change in relative peak intensities when the concentration is varied). As indicated in Fig. 3 by the dashed line, two separate band emissions are evident for both samples. The first band emission encountered (at high energy levels) is the near-band gap emission (NBE) and in our case presents a double peak at 385 and 409 nm for the sonochemical sample, while the hydrothermal ZnO rods NBE peak positions are at 388 and 409 nm. The first of the two peaks is actually in the ultraviolet luminescence (UVL), while the second one represents the blue luminescence (BL). The UVL for the sonochemical rods has a full width at half maximum (FWHM) of 43 nm, i.e., a ΔE of approximately 0.35 eV, while for the hydrothermal rods the FWHM of the UVL is of 34 nm, i.e., a ΔE of approximately 0.28 eV. The BL peak has a FWHM of 23 nm, i.e., a ΔE of approximately 0.16 eV, for the sonochemical ZnO, while the BL FWHM for the hydrothermal ZnO is 20 nm, i.e., a ΔE of 0.14 eV. As it can be appreciated, both UVL and BL peaks are slightly narrower in the hydrothermal ZnO rods case. The band gap energy of ZnO is 3.37 eV, corresponding to 360 nm. The second band emission is the so-called subband gap emission (SBE). The emission maximum is at 587 nm for the sonochemical ZnO and 569 nm for the hydrothermal rods. In this case the half maximum width is of 119 nm, i.e., a ΔE of 0.43 eV for the sonochemical sample and 131 nm, i.e., a ΔE of 0.46, for the hydrothermal rods. This time, the latter sample shows a broader peak than the sonochemical ZnO rods. It has been shown that the width of the visible peak, at least for yellow-redshifted peaks, can be directly associated with inhomogeneities within single rods rather than morphology discrepancies among different

FIG. 4. A simplified ZnO (sonochemical) band gap showing the different emission associated with various defects. As example, the wavelengths of the sonochemical ZnO sample are indicated.

rods.¹⁹ Comparing the value calculated for the SBE peaks in our case, with values reported in literature for solution-grown ZnO rods,¹⁹ these relatively narrow ranges seem to indicate that the rods are structurally homogeneous. The attribution of these bands (NBE and SBE) to the intrinsic defects of the undoped ZnO gives us an interesting insight into the rich defect chemistry of this oxide.

A thorough understanding of the correlation between defects and their associate charge carriers with the material properties is necessary to achieve successful applications of ZnO structures. Although ZnO defects have been studied in the past,²⁰ a similar approach is still largely lacking for the novel structures available today.⁹ Native defects in undoped ZnO are donorlike in nature and, therefore, the material has *n*-type conductor characteristics. A particular aspect that needs also to be taken in consideration is that defects might be aliovalent (i.e., they have different ionization degrees). For ZnO, the donor defects are due to interstitial zinc and oxygen vacancies. Accordingly the well-known Kröger-Vinch notation,²¹ we will hereafter refer to them as Zn_i and V_O , respectively. Because both types of defect tend to donate two electrons each, it is difficult to distinguish their contribution through electrical measurements. However, it has been shown that it is possible to correlate defect spectral features with properties such as conductivity and, therefore, discriminate the contribution of one defect from the others.²² In Fig. 4, a simplified and general model of the band gap of the ZnO is shown. Only in the case of the V_O , two different degrees of ionization have been considered (charge and number of charges are indicated by the subscripted terms). In addition to the already stated donor defects Zn_i and V_O , the acceptorlike defects O_i (interstitial oxygen) and V_{Zn} (zinc vacancy) are also taken into account. For the sake of space they fictionally share the same energy level although it should be clear that they do have in reality separate levels. As illustrated in Fig. 4, the UVL is due to an energetic transition from the level occupied by Zn_i to the valence band, while the BL can be attributed to an energy exchange between the V_O^- and the valence band. We arrive at this conclusion by carefully comparing the spectral features given in Fig. 3 with known ZnO band gaps discussed in the literature.^{9,20} Although some discrepancies in the absolute

positions of the defect energy levels were observed, the relative position of the defect levels is consistent with those previously reported. The attribution of the green luminescence (GL) to the oxygen vacancy is widely accepted, although the contribution of the bulk defects versus the defects on the ZnO surface is still debated.^{12,19} We attribute GL to the transition occurring between the energy level occupied by V_O^{2-} and the valence band. As it can be observed from Fig. 3, neither the sonochemical nor the hydrothermal ZnO rod spectra present a well-defined green peak and this is somehow to be expected at room temperature.²³ Instead, the sub-band gap is spread over a relative large range (from 450 to 700 nm approximately). The peak itself of this band is shifted toward the yellow region at 587 nm for the sonochemical ZnO rods and 569 nm for the hydrothermal sample. Yellow luminescence (YL) has been reported to be temperature dependent according to the equation $E_{eA} = E_{gap} - E_A + 0.5 kT$, where k is the Boltzmann constant, T is the temperature, E_{gap} is the band gap energy, and E_A is the acceptor binding energy.²² The calculated E_A is in our case of 1.345 eV for the sonochemical sample and 1.275 eV for the hydrothermal ZnO rods. An increase in YL intensity indicates an increase in the acceptorlike defects [i.e., an increase in interstitial oxygen O_i and/or zinc vacancy V_{Zn} (Ref. 22)] that will compensate the effect of the native *n*-type doping and consequently will affect the conductivity of the ZnO structure. Although, in Fig. 4, a transition between the conduction band and the O_i or V_{Zn} (or both) is indicated, inter-band transitions between donor defects and acceptor defects cannot at this stage be ruled out (in this case the energy level associated with O_i or V_{Zn} in Fig. 4 should be shifted toward the valence band). The influence of acceptor-like defects turns out to be very relevant in our case because from Fig. 3, we note that the intensity of the YL peak is much higher for the hydrothermal ZnO than for the sonochemical sample (we also notice a decrease in the intensity for UVL and BL peaks as well as for sonochemical ZnO rods). This seems to indicate that sonochemical ZnO rods are crystals with fewer defects in comparison with the hydrothermal sample. One of the best indications of the quality of the crystals comes from the analysis of the intensity ratio between the sum of GL and BL (the green component of the sub-band-edge emission) and the UVL intensity [(BL+GL)/UVL]. An increase in this ratio indicates a decrease in the resistivity of ZnO.²² Although no clear GL peak can be recognized, there is undoubtedly a green component in the SBE. Taking into account the intensity at 520 nm for both spectra, the ratio goes from 0.93 for the sonochemical rods to 1.31 for the hydrothermal ZnO. This, in agreement with the previous discussions on the intensity of YL, indicates that the sonochemical method is likely to produce crystals of higher quality. The fluorescence data show that the nature and density of the defects are different, and this in turn could influence the future doping strategies of the ZnO rods. Although further research is necessary to understand this phenomenon—and we are already envisaging, for example, a photoluminescence study as a function of temperature—we already notice that in the sonochemical method, the sonolysis of water in oxygen gas and hydrogen peroxide creates an oxygen rich

FIG. 5. (a) Variation in the sonochemical ZnO rod peak intensity as a function of the sonoprobe amplitude. The fitted curves are shown as guide to the eye (dotted lines for the UVL peak and dashed-dot and dashed for BL and YL peaks, respectively). (b) Normalized YL/UVL intensity—taking into account yield discrepancies—vs the ultrasonic probe amplitude. A fitted curve is shown as guide for the eyes, clearly showing an optimum minimum.

environment. This extra oxygen should also be taken into consideration in the formation of the ZnO crystals. This and other differences in the number and volumes of elements involved in the crystal formation or in growth parameters, such as local temperature and pressure, are likely candidates to explain the differences in crystal structure obtained by the two growth methods.

In an attempt to understand the influence of the ultrasonic power transferred to the reacting solution over the crystal quality, we undertook a systematic study in which consistent volumes and concentrations (15 ml, $10^{-3}M$) of zinc nitrate and HMTA were exposed to a range of ultrasonic powers. The microsonoprobe amplitude was varied between 20% and 40% of the maximum value. Synthesized ZnO rods were then allowed to precipitate due to gravity over 24 h, washed in ultrapure water, then centrifuged and resuspended in isopropanol. Finally, fluorescence spectra for each sample were recorded. The final solutions are stable over several hours and are easily redispersed by brief ultrasonification. In Fig. 5(a) a summary of the results is presented. The absolute

intensity of the three major peaks—UVL, BL, and YL—has been plotted against the sonoprobe amplitude, expressed as percentage of the maximum value. To normalize the results obtained against variations in the synthesis yield, we plotted the ratio YL/UVL against the sonoprobe amplitude. As shown in Fig. 5(b), a fitted minimum is found at around 35%. This indicates that around this value the quality of the crystal reaches a relative optimum. This is likely to be associated with factors like an increase in the heat transferred to the reacting solution. A further increase in the ultrasound power is likely to affect the morphology of the rods damaging the outer surface of the freshly formed ZnO rods. Through SEM studies, it was possible to observe that the dimensions of the rods tend to be more homogeneous when an amplitude of 20%–30% is used. At 35% we start to notice occasional larger rods, while at 40% there is quite a large variation in sizes and morphologies, with almost all of them presenting an irregular outer surface.

IV. CONCLUSIONS

In conclusion, we have shown that a fast sonochemical synthesis of wurtzite ZnO rods, over 15 times faster than previously reported, can be achieved by placing the vial containing the reacting solution in a simple thermal bath to control the temperature drop in a preheated zinc nitrate and HMTA solution. By comparing the luminescence spectra of these rods with that of ZnO structures synthesized by the more established (and time-consuming) hydrothermal method, we have shown that in the sonochemical sample the crystal quality is higher perhaps due to an oxygen rich environment. The presence of a higher number of acceptorlike defects in the hydrothermal ZnO rods is likely to have a direct influence on rod electronic properties. We also prove that the intensity of the ultrasonic power transferred to the reacting medium has a marked influence on the crystal quality. Both methods are inexpensive routes to scale up the generation of ZnO thin films and structures at moderate temperatures with controlled complexity. This study has given an insight into the defects chemistry associated with these two aqueous-solution growth methods. A better understanding of the crystal defects and their influence on ZnO rod properties is essential for achieving successful applications of these materials.

ACKNOWLEDGMENTS

The authors wish to thank the EPSRC, U. K. for funding via a Portfolio Partnership Award.

- ¹M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science* **292**, 1897 (2001).
- ²J. Bao, M. A. Zimmmer, F. Capasso, X. Wang, and Z. F. Ren, *Nano Lett.* **6**, 1719 (2006).
- ³A. M. Peiró, P. Ravirajan, K. Govender, D. S. Boyle, P. O'Brien, D. D. C. Bradley, J. Nelson, and J. R. Durrant, *J. Mater. Chem.* **16**, 2088 (2006).
- ⁴J. Suehiro, N. Nakagawa, S. Hidaka, M. Ueda, K. Imasaka, M. Higashihata, T. Okada, and M. Hara, *Nanotechnology* **17**, 2567 (2006).
- ⁵J. H. Song, J. Zhou, and Z. L. Wang, *Nano Lett.* **6**, 1656 (2006).
- ⁶J. X. Wang, X. W. Sun, Y. Yang, H. Huang, Y. C. Lee, O. K. Tan, and L. Vayssieres, *Nanotechnology* **17**, 4995 (2006).
- ⁷S. J. Henley, M. N. R. Ashfold, and D. Cherns, *Thin Solid Films* **422**, 69 (2002).

- ⁸S. J. Henley, M. N. R. Ashfold, D. P. Nicholls, P. Wheatley, and D. Cherns, *Appl. Phys. A: Mater. Sci. Process.* **79**, 1169 (2004).
- ⁹L. S. Schmidt-Mende and J. L. MacManus-Driscoll, *Mater. Today* **10**, 40 (2007).
- ¹⁰L. Vayssieres, *Adv. Mater. (Weinheim, Ger.)* **15**, 464 (2003).
- ¹¹K. Govender, D. S. Boyle, P. O'Brien, D. Binks, D. West, and D. Coleman, *Adv. Mater. (Weinheim, Ger.)* **14**, 1221 (2002).
- ¹²X. L. Hu, Y. J. Zhu, and S. W. Wing, *Mater. Chem. Phys.* **88**, 421 (2004).
- ¹³S. H. Jung, E. Oh, K. H. Lee, W. Park, and S. H. Jeong, *Adv. Mater. (Weinheim, Ger.)* **19**, 749 (2007).
- ¹⁴T. J. Mason, *Practical Sonochemistry* (Ellis Horwood, Chichester, 1991), p. 186.
- ¹⁵R. T. R. Kumar, E. McGlynn, C. McLoughlin, S. Chakrabarti, R. C. Smith, J. D. Carey, J. P. Mosnier, and M. O. Henry, *Nanotechnology* **18**, 6 (2007).
- ¹⁶D. A. Schwartz, K. R. Kittilstved, and D. R. Gamelin, *Appl. Phys. Lett.* **85**, 1395 (2004).
- ¹⁷N. S. Norberg, K. R. Kittilstved, J. E. Amonette, R. K. Kukkadapu, D. A. Schwartz, and D. R. Gamelin, *J. Am. Chem. Soc.* **126**, 9387 (2004).
- ¹⁸D. A. Schwartz, N. S. Norberg, Q. P. Nguyen, J. M. Parker, and D. R. Gamelin, *J. Am. Chem. Soc.* **125**, 13205 (2003).
- ¹⁹J. W. P. Hsu, D. R. Tallant, R. L. Simpson, N. A. Missert, and R. G. Copeland, *Appl. Phys. Lett.* **88**, 3 (2006).
- ²⁰F. A. Kroger, *Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1964).
- ²¹F. A. Kroger and H. J. Vink, *Solid State Phys., Adv. Res. Appl.* **3**, 307 (1956).
- ²²Y. J. Lin, C. L. Tsai, Y. M. Lu, and C. J. Liu, *J. Appl. Phys.* **99**, 093501 (2006).
- ²³S. L. Shi, G. Q. Li, S. J. Xu, Y. Zhao, and G. H. Chen, *J. Phys. Chem. B* **110**, 10475 (2006).