

## Temperature dependence of weak localization effects of excitons in ZnCdO/ZnO single quantum well

W. F. Yang,<sup>1,a)</sup> R. Chen,<sup>1</sup> B. Liu,<sup>1</sup> L. M. Wong,<sup>2</sup> S. J. Wang,<sup>2</sup> and H. D. Sun<sup>1,b)</sup>

<sup>1</sup>*Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371*

<sup>2</sup>*Institute of Materials Research and Engineering, A\*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602*

(Received 21 March 2011; accepted 22 April 2011; published online 7 June 2011)

We report on the optical properties of high-quality ZnCdO/ZnO single quantum well (SQW) grown on *c*-sapphire substrates by pulsed laser deposition. The temperature dependent photoluminescence (PL) of ZnO/ZnCdO SQWs exhibits an inconspicuous S-shaped property due to the weak carrier localization effect, as a consequence of the slightly inhomogeneous Cd distribution in the well layer as well as the smooth interfaces. The integrated PL intensity of the higher Cd SQW decreases faster than that of the lower sample with increasing temperature, indicating the presence of interface barrier in high Cd content SQWs. © 2011 American Institute of Physics. [doi:10.1063/1.3592887]

### I. INTRODUCTION

Recently, ZnO related materials are attracting much attention as promising candidates for optoelectric applications in visible and ultraviolet (UV) regions.<sup>1–5</sup> Compared with other wide bandgap materials, ZnO has larger exciton binding energy (~60 meV), which permits excitonic recombination even at room temperature.<sup>6,7</sup> In fact, the enhancement of excitation binding energy of ZnO has been observed in ZnMgO/ZnO multiple quantum well (MQW),<sup>8</sup> which is favorable for the stability of exciton states in UV lasing application. Redshift of the luminescence peak with respect to that of ZnO can be realized by alloying ZnO with CdO. Previously, ZnCdO epilayers and ZnCdO/ZnO QWs have been mainly prepared by molecular beam epitaxy and metal-organic epitaxial methods.<sup>9–13</sup> However, fabrication of ZnCdO films and heterostructures by pulsed laser deposition (PLD) is rarely reported.<sup>5,14–17</sup> Recent works on the optical properties of GaN-based QWs have shown that localized exciton transitions always dominate in this system at low temperatures<sup>18,19</sup> and the degree of carrier localization is strongly correlated with the composition concentrations, well width, and interface roughness.<sup>20,21</sup> The understanding of carrier dynamics is essential for the lasing application. However, so far there have been only very few published studies on ZnCdO/ZnO MQWs. On the other hand, for MQWs, information about the electronic structure and carrier dynamics may be obscured by multiple different QWs, thus investigation of ZnCdO/ZnO single quantum well (SQW) should provide a clearer picture of understanding the recombination mechanism in these structures.

In this letter, we report the photoluminescence (PL) characterization of two ZnCdO/ZnO SQWs of different Cd content grown on sapphire substrates by PLD. Temperature dependence of weak localization effects of excitons in both

ZnCdO/ZnO SQWs indicates slightly inhomogeneous Cd distribution has been achieved in the ultrathin ZnCdO well layers.

### II. EXPERIMENTAL DETAILS

ZnCdO/ZnO SQWs were prepared on *c*-plane sapphire substrates by PLD method in an ultrahigh vacuum chamber. A KrF excimer laser (248 nm, 320 mJ, 20 Hz, 25 ns) was used as ablating source and two ceramic targets of ZnO and Zn<sub>0.7</sub>Cd<sub>0.3</sub>O were used. The two ZnCdO/ZnO SQWs with the same well width of 2.6 nm but different Cd contents were fabricated. The SQWs consist of a 10 nm ZnO buffer layer, a ZnO barrier layer with thickness of 90 nm, a 2.6 nm ZnCdO well layer, and a ZnO cap layer thickness of 10 nm. Details of the growth procedure and the bandgap energy in ZnCdO have been given elsewhere.<sup>17</sup> In order to control the Cd content in the well layers, ZnCdO well layers were grown at low substrate temperature of 310 for sample A and 250°C for sample B, respectively. The subsequent postdeposition annealing treatment *in situ* at 650°C for 20 min was carried out to improve the interface between ZnO barriers and ZnCdO well layer. The Cd contents were determined by energy-dispersive x-ray spectroscopy analysis from ZnCdO films. The barrier and well layer thicknesses were determined by prescribed deposition time. The PL spectra were performed by excitation from a 325 nm line of a He–Cd laser.

### III. RESULTS AND DISCUSSION

Figure 1 shows the room temperature PL spectra of the two ZnCdO/ZnO SQW structures with the same well width of 2.6 nm but different Cd contents of (A) 6.1 and (B) 7.9%. The inset is the PL spectra of the two SQWs obtained at 10 K. Judging from the peak positions at 300 K, peaks at 3.06 (sample A) and 3.0 eV (sample B) are from the exciton transition confined in ZnCdO well layers and the peaks emission around 3.28 eV correspond to the emissions from ZnO barrier layers. Note that, compared with the PL emission from single ZnCdO

<sup>a)</sup>Electronic mail: wfyang@yahoo.com.

<sup>b)</sup>Electronic mail: hdsun@ntu.edu.sg.

alloy layer with the same Cd content, the peak from the QW-related emission in Fig. 1 has a slightly higher energy due to the presence of quantum confinement effect. On the other hand, it is well known that the Cd content strongly influences the quantum yield and shifts the PL position. Low-energy shifts of the well layer PL features occurring for higher Cd content with the same well thickness signifies the clear shrinkage of optical bandgap by higher Cd content. On the low energy side, a broad band defect-related luminescence around 2.3 eV from both samples was observed, which is related to deep level defects. These deep levels are most probably due to oxygen vacancies or zinc interstitials<sup>22,23</sup> which should be the dominating sources of the defect emission for the SQW analyzed in this work. In the inset of Fig. 1 (10 K), we ascribe the PL peak near 3.37 eV to free exciton ( $FX_A$ ), the PL peak near 3.35 eV to the excitons bound to neutral donors (denoted by  $D^0X$ ), and the PL peak near 3.32 eV to the electron satellite transition (EST) in the ZnO barriers, which we will discuss below in details. On the other hand, the spectrally integrated yield of the two SQWs emission is even much larger than that from the ZnO barriers with about 40 times larger in total thickness, both at low and room temperatures. This high-efficiency relaxation from barriers to well layers implies that high-quality ZnCdO/ZnO SQWs have been achieved by PLD. However, it has been recognized that CdO assumes the rock-salt structure, which is dissimilar to the wurtzite structure of ZnO. Thus, the growth of higher Cd content well layer with high crystalline quality is rather difficult and it usually produces defects in the well layer and interface barrier between the well and barriers caused by the complication of lattice mismatch. This is in good agreement with the results that the defect-related emission from the higher Cd sample B is stronger than from sample A, while the QW-related emission from sample B is weaker than from sample A. On the other hand, the low-temperature width of this QW emission is as small as 106 and 79 meV for sample A and sample B, respectively, which is much smaller than QWs of comparable structures grown on a-plane sapphire substrates

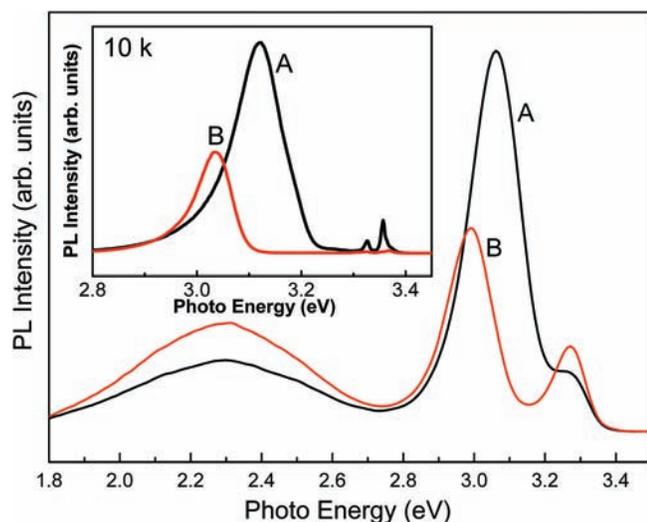


FIG. 1. (Color online) PL spectra of ZnCdO/ZnO SQWs measured at room temperature and 10 k (inset). Sample A and B with the various Cd contents in  $Zn_{1-x}Cd_xO$  well layer of 6.1 and 7.9% are shown.

by molecular beam epitaxy.<sup>24</sup> It is known that narrow lines in luminescence of quantum well excitons at low temperatures implies high quality of quantum well interfaces.<sup>25</sup> All these results indicate that the high-quality ZnCdO/ZnO SQW with smooth interfaces have been achieved in our case.

For the QW luminescence, a strong localization effect of excitons is expected due to local fluctuations of the bandgap energy in the ternary alloy. The normalized PL spectra of sample A and B measured in the temperature range between 10 and 300 K are presented in Fig. 2. However, it is interesting to note that the temperature dependent PL of ZnO/ZnCdO SQWs exhibits an inconspicuous S-shaped property due to the weak carrier localization effect. Taking sample B for example, as the temperature increases from 10 to 120 K, the peak energy ( $E_p$ ) redshifts 18 meV. However, from 120 to 140 K the  $E_p$  of PL blueshifts 2 meV. When the temperature is further increased above 140 K, the  $E_p$  decreases again. A typical S-shaped behavior has been observed previously in the GaN-based QW structures with strong carrier localization effect,<sup>21</sup> as well as in the ZnO/ZnCdO/ZnO double heterostructures with  $\sim 10$  nm thick ZnCdO alloys,<sup>16</sup> which is ascribed to the potential fluctuation, as a consequence of the inhomogeneous alloy composition and roughness interfaces. In general, at the lowest temperature, the photogenerated carriers (excitons) are potential minima and rapidly captured in their lifetime by the localized potential induced by the fluctuation of alloy composition. An increase in the temperature increases the thermal energy of charge carriers, eventually enough to delocalize. Here we must mention that the peak energy of PL blueshifts less than 4 meV for two ZnCdO/ZnO SQWs, which is greatly less than the previous results of 22 meV for ZnCdO/ZnO coaxial MQW nanowires<sup>26</sup> and  $\sim 20$  meV for ZnO/ZnCdO/ZnO double heterostructures.<sup>16</sup> As we mentioned above, the degree of carrier localization is strongly correlated with the spatial potential fluctuations caused by the inhomogeneous alloy distribution or roughness interfaces in QWs. Our previous

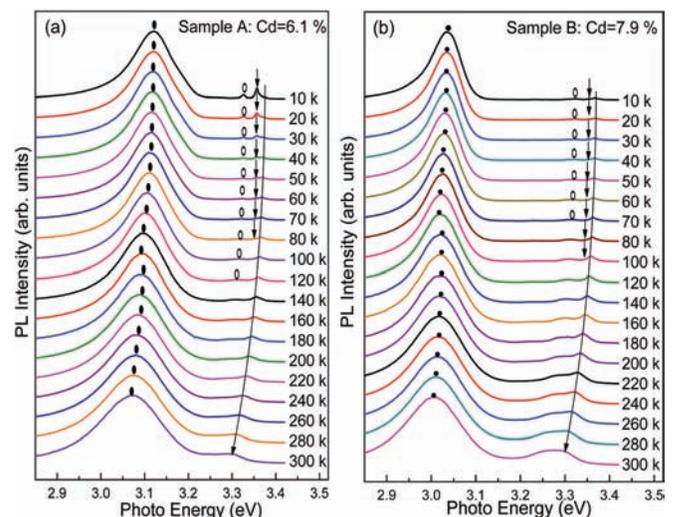


FIG. 2. (Color online) Temperature-dependent PL spectra for (a) sample A: Cd = 6.1% and (b) sample B: Cd = 7.9% measured by a He-Cd laser. The closed circles indicate the peak evolution of the QW related emission. The open circles denote EST peak, the arrows show the trend of  $D^0X$ , and the solid line indicates the peak evolution of the  $FX_A$  emission of ZnO barriers.

results<sup>17</sup> show that atomically flat surface is formed on the SQWs and the root mean square roughness over a scan area of  $3 \times 3 \mu\text{m}^2$  is  $\sim 0.26$  nm, indicating smooth and high quality interfaces in the SQWs. Hence, the small shifts in our case, namely the weak carrier localization effect, is proposed to be ascribed to a combined effect of the slightly inhomogeneous Cd distribution in the ZnCdO well layer and the smooth interfaces between the well and ZnO barriers.

Figure 3 shows the variation of the PL peak energies of the ZnCdO/ZnO SQWs as a function of temperature. It was found that the  $\text{FX}_A$ ,  $\text{D}^0\text{X}$ , and EST peak energies show a monotonic redshift with increasing temperature. The  $\text{FX}_A$  peak energy decreases monotonically with increasing temperature, which can be well described by the empirical Varshni equation

$$E(T) = E(0) - \frac{\alpha T^2}{\beta + T}, \quad (1)$$

where  $E(0)$  is the excitonic bandgap at 0 K, and  $\alpha$  and  $\beta$  are the corresponding thermal coefficients. The close squares in Fig. 3 are the experimental data of  $\text{FX}_A$  peak energy and the black lines are the fitting curve obtained by using the Varshni's equation. It is clearly shown that the curves from two samples fit our experimental data very well and the temperature dependent PL peak for the  $\text{FX}_A$  emission of ZnO barriers is consistent with the estimated energy decrease of about  $\sim 70$  meV at 300 K. The value of  $E(0)$  obtained from the fittings is 3.371 eV for sample A and 3.367 eV for sample B, respectively.

Figure 4 shows the integrated PL intensity of the SQW-related emission in the SQWs as a function of temperature from 10 to 300 K. As we mentioned above, the intensity of the ZnCdO QW-related emission decrease remarkably with increasing temperature, which is partly due to the increased nonradiative recombination. The internal quantum efficiency ( $\eta_{\text{int}}$ ) of ZnCdO/ZnO SQWs was estimated by comparing PL intensities assuming that the  $\eta_{\text{int}}$  is 100% at low temperature (10 K) regardless of excitation carrier density.<sup>27</sup> As the inset of Fig. 4 shows, the  $\eta_{\text{int}}$  of SQW with higher Cd and lower

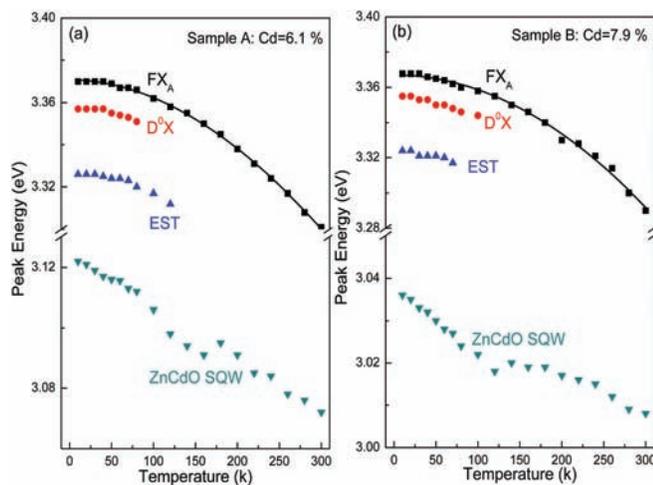


FIG. 3. (Color online) Temperature dependent peak positions of  $\text{FX}_A$ ,  $\text{D}^0\text{X}$ , EST, and QW of (a) sample A and (b) B, respectively. The solid line is the fitting curve of the experimental data according to the Varshni equation.

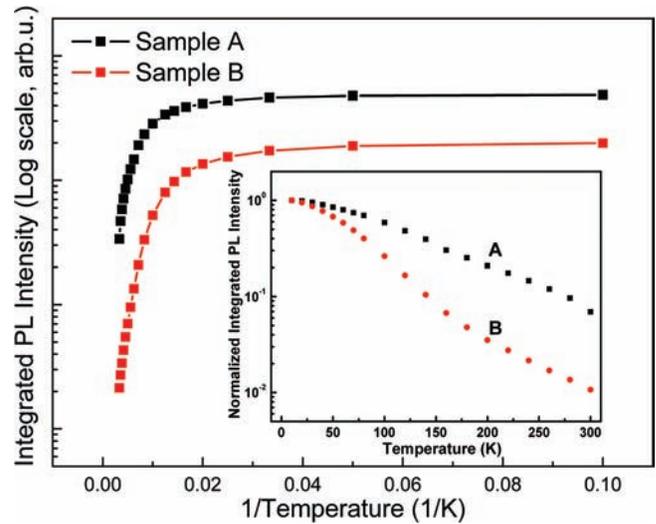


FIG. 4. (Color online) Temperature dependence of the integrated PL intensity and the normalized integrated PL intensity (the inset) for the two SQWs.

Cd at 300 K was 1.1% and 6.9%, respectively, which indicates that there are some physical mechanisms responsible for this distinction of  $\eta_{\text{int}}$  in the two SQWs. Here we deduced that one possible reason is the optical properties of ZnCdO well layer in lower Cd sample A is better than that of sample B. As we mentioned above, the ZnCdO well layer in the sample A and sample B is grown at low substrate temperature of 310 and 250°C, respectively. Due to the low mobility of atoms at lower temperature, the quality of the ZnCdO layer in higher Cd sample B is not good as sample A. Moreover, it is shown that the integrated PL intensity of sample A is larger than that of sample B at all temperatures, which provide another evidence that the optical properties of ZnCdO well layer in lower Cd sample A is better than that of sample B. On the other hand, it can be seen from the Fig. 4 that the integrated PL intensity of the higher Cd sample B decreases faster than that of sample A with increasing temperature. As we mentioned above, it usually produces interface barrier between the well and barrier layer caused by lattice mismatch. Since both a- and c-lattice constants were monotonically increasing functions of Cd content<sup>28</sup> and the presence of interface barrier in the SQWs is related to lattice mismatch, it is reasonable to deduce that the interface barrier height ( $\Delta\Phi$ ) of the lower Cd sample A is smaller than that of the higher Cd sample B, due to the lower lattice mismatch. Hence, an increase in the temperature increases the thermal energy of carriers, eventually enough to surmount obstacles of the interface and relax into well, which compensate the decrease of radiative recombination with increasing temperature.

#### IV. CONCLUSION

In summary, we have studied the optical properties of ZnCdO/ZnO SQWs on sapphire substrates prepared by PLD. Temperature dependent PL measurement was performed from 10 to 300 K to study carrier localization effect and evolution of the peaks in the SQWs. Temperature dependence of the exciton emission peak energy from the ZnCdO/ZnO SQWs shows a weak localization effect, which is proposed to

be related to the slightly inhomogeneous Cd distribution in the ZnCdO well layer and the smooth interfaces between the well and ZnO barriers. The integrated PL intensity of the higher Cd SQW decreases faster than that of the lower sample with increasing temperature, which indicates the presence of interface barrier in the SQWs is related to Cd contents.

## ACKNOWLEDGMENTS

Support from the Singapore MOE under Project No. RG40/07 and RG63/10 are acknowledged.

- <sup>1</sup>J. M. Qin, B. Yao, Y. Yan, J. Y. Zhang, X. P. Jia, Z. Z. Zhang, B. H. Li, C. X. Shan, and D. Z. Shen, *Appl. Phys. Lett.* **95**, 022101 (2009).
- <sup>2</sup>A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, *Nat. Mater.* **4**, 42 (2005).
- <sup>3</sup>Z. P. Wei, Y. M. Lu, D. Z. Shen, Z. Z. Zhang, B. Yao, B. H. Li, J. Y. Zhang, D. X. Zhao, X. W. Fan, and Z. K. Tang, *Appl. Phys. Lett.* **90**, 042113 (2007).
- <sup>4</sup>B. P. Zhang, N. T. Binh, K. Wakatsuki, C. Y. Liu, and Y. Segawa, N. Usami, *Appl. Phys. Lett.* **86**, 032105 (2005).
- <sup>5</sup>H. D. Sun, T. Makino, N. T. Tuan, Y. Segawa, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, *Appl. Phys. Lett.* **77**, 4250 (2000).
- <sup>6</sup>S. Sadofev, S. Kalusniak, J. Puls, P. Schäfer, S. Blumstengel, and F. Henneberger, *Appl. Phys. Lett.* **91**, 231103 (2007).
- <sup>7</sup>T. Makino, Y. Segawa, M. Kawasaki, and H. Koinuma, *Semicond. Sci. Technol.* **20**, S78 (2005).
- <sup>8</sup>H. D. Sun, T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, *J. Appl. Phys.* **91**, 1993 (2002).
- <sup>9</sup>A. V. Thompson, C. Boutwell, J. W. Mares, and W. V. Schoenfeld, A. Osinsky, B. Hertog, J. Q. Xie, S. J. Pearton, and D. P. Norton, *Appl. Phys. Lett.* **91**, 201921 (2007).
- <sup>10</sup>I. A. Buyanova, X. J. Wang, G. Pozina, W. M. Chen, W. Lim, D. P. Norton, S. J. Pearton, A. Osinsky, J. W. Dong, and B. Hertog, *Appl. Phys. Lett.* **92**, 261912 (2008).
- <sup>11</sup>X. J. Wang, I. A. Buyanova, W. M. Chen, M. Izadifard, S. Rawal, D. P. Norton, S. J. Pearton, A. Osinsky, J. W. Dong, and A. Dabiran, *Appl. Phys. Lett.* **89**, 151909 (2006).
- <sup>12</sup>J. Ishihara, A. Nakamura, S. Shigemori, T. Aoki, and J. Temmyo, *Appl. Phys. Lett.* **89**, 091914 (2006).
- <sup>13</sup>S. Kalusniak, S. Sadofev, J. Puls, and F. Henneberger, *Laser & Photon. Rev.* **3**, 233 (2009).
- <sup>14</sup>W. F. Yang, R. Chen, B. Liu, G. G. Gurzadyan, L. M. Wong, S. J. Wang, and H. D. Sun, *Appl. Phys. Lett.* **97**, 061104 (2010).
- <sup>15</sup>H. S. Kang, J. W. Kim, J. H. Kim, S. Y. Lee, Y. Li, Jang-Sik Lee, J. K. Lee, M. A. Nastasi, S. A. Crooker, and Q. X. Jia, *J. Appl. Phys.* **99**, 066113 (2006).
- <sup>16</sup>M. Lange, J. Zippel, G. Benndorf, C. Czekała, H. Hochmuth, M. Lorenz, and M. Grundmann, *J. Vac. Sci. Technol. B* **27**(3), 1741 (2009).
- <sup>17</sup>W. F. Yang, B. Liu, R. Chen, L. M. Wong, S. J. Wang, and H. D. Sun, *Appl. Phys. Lett.* **97**, 061911 (2010).
- <sup>18</sup>J. H. Na, R. A. Taylor, K. H. Lee, T. Wang, A. Tahraoui, P. Parbrook, A. M. Fox, S. N. Yi, Y. S. Park, J. W. Choi, and J. S. Lee, *Appl. Phys. Lett.* **89**, 253120 (2006).
- <sup>19</sup>H. Schömig, S. Halm, A. Forchel, G. Bacher, J. Off, and F. Scholz, *Phys. Rev. Lett.* **92**, 106802 (2004).
- <sup>20</sup>A. Bell, S. Srinivasan, C. Plumlee, H. Omiya, F. A. Ponce, J. Christen, S. Tanaka, A. Fujioka, and Y. Nakagawa, *J. Appl. Phys.* **95**, 4670 (2004).
- <sup>21</sup>Y. H. Cho, G. H. Gainer, A. J. Fischer, J. J. Song, S. Keller, U. K. Mishra, and S. P. DenBaars, *Appl. Phys. Lett.* **73**, 1370 (1998).
- <sup>22</sup>S. Monticone, R. Tufeu, and A. V. Kanaev, *J. Phys. Chem. B* **102**, 2854 (1998).
- <sup>23</sup>Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, and V. Avrutin, *J. Appl. Phys.* **98**, 041301 (2005).
- <sup>24</sup>S. Sadofev, S. Blumstengel, J. Cui, J. Puls, S. Rogaschewski, P. Schäfer, and F. Henneberger, *Appl. Phys. Lett.* **89**, 201907 (2006).
- <sup>25</sup>A. L. Efros and M. E. Raikh, *Optical Properties of Mixed Crystals* (North-Holland, Amsterdam, 1988).
- <sup>26</sup>C. Cheng, B. Liu, E. J. Sie, W. Zhou, J. Zhang, H. Gong, C. H. A. Huan, T. C. Sum, H. D. Sun, and H. J. Fan, *J. Phys. Chem. C* **114**, 3863 (2010).
- <sup>27</sup>K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, and A. Scherer, *Nat. Mater.* **3**, 601 (2004).
- <sup>28</sup>T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, R. Shiroki, K. Tamura, T. Yasuda, and H. Koinuma, *Appl. Phys. Lett.* **78**, 1237 (2001).