

Correlations between the band structure, activation energies of electron traps, and photoluminescence in n-type GaNAs layers

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(Received 27 March 2012; accepted 8 August 2012; published online 23 August 2012)

It has been observed that activation energies of electron traps in GaNAs layers of various nitrogen concentrations vary consistently if the N-related changes in the band structure of GaNAs and energy positions of donor levels are plotted relative to the valence band edge on the same diagram. Within this diagram, it is expected that the activation energy of electron traps of the same microscopic nature should decrease with the increase of nitrogen concentration. The identification of electron traps in GaNAs within the proposed diagram allows to interpret the broad emission at ~ 0.9 eV as the donor trap–valence band and the donor acceptor pair recombination involving of these traps. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4747504>]

The incorporation of nitrogen atoms into GaAs leads to a remarkable band-gap reduction, which originates mainly from a downward of the conduction band edge.^{1,2} Because of this feature, GaNAs as well as other III-V-N alloys are promising candidates for various optoelectronic applications including solar cells and GaAs-based telecommunication laser diodes.¹ Unfortunately, it is also observed that the optical quality of III-V-N alloys deteriorates drastically with the increase of nitrogen concentration indicating that N-related point defects could be responsible for the poor optical quality of III-V-N alloys. The electronic nature of N-related defects and their influence on photoluminescence (PL) properties are still under debate.^{3–6} The deep level transient spectroscopy (DLTS) and Laplace-transform deep-level spectroscopy (LTDLS)⁷ are powerful electrical diagnostic tools to study point defects in semiconductors. These techniques have been applied to study activation energies as well as capture cross sections and concentrations of point defects in bulk GaNAs.^{8–11} These investigations clearly confirmed that the incorporation of N atoms into GaAs leads to the formation of electron and hole traps, which are not observed in GaAs. However, there have been no systematic studies on the dependence of the properties of these traps in the GaNAs films with changing N concentration. The aim of this work is to establish relationships between the band structure, activation energies of electron traps, and defect-related PL in GaNAs layers with various nitrogen concentrations.

GaNAs layers of various nitrogen concentrations ranging from 0.2% to 1.2% were grown by molecular beam epitaxy on n^+ GaAs substrates at 500 °C. A highly silicon doped ($2 \times 10^{18} \text{ cm}^{-3}$) buffer layer of 0.1 μm thickness was deposited directly on n^+ GaAs substrate. Next, 1 μm thick GaAsN epilayer slightly doped by silicon ($3 \times 10^{16} \text{ cm}^{-3}$) was deposited on this buffer.

In order to investigate the N-related reduction of energy gap in GaNAs, the contactless electroreflectance (CER) spectroscopy has been applied.¹² Since this technique is sensitive to large changes in the optical absorption, it is not affected by any point defects and therefore is a very good tool to determine the energy gap at $k=0$. Figure 1 shows CER spectra measured at room temperature for four GaNAs layers of various compositions. As expected, the CER

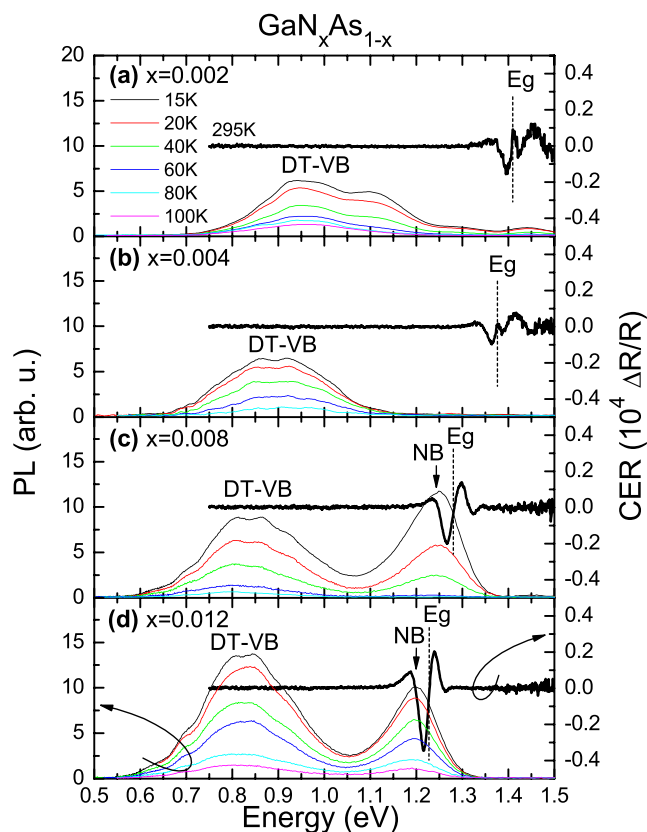


FIG. 1. Room temperature CER and low temperature PL spectra of n-type $\text{GaN}_x\text{As}_{1-x}$ layers of various nitrogen concentrations.

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resonance shifts to red with increasing N concentration. A standard approach has been applied to determine the band gap by fitting the experimental data.¹² The room temperature energy gaps of 1.4, 1.38, 1.28, and 1.22 eV were found for GaNAs layers with 0.2%, 0.4%, 0.8%, and 1.2% N content, respectively. The obtained N-dependence of the energy gap is in a good agreement with the reported experimental data¹³ and the band anticrossing (BAC) model.²

In contrast to CER spectroscopy, the PL technique is very sensitive to point defects, and therefore, the PL spectra of GaNAs are often dominated by a defect-related emission at low temperatures.³ Such a situation also takes place for the four GaNAs layers (see PL spectra in Fig. 1). In this case, two PL bands (DT-VB and NB) are clearly visible in these spectra. The energy of the PL bands indicates that they can be attributed to deep levels inside the energy gap. However, their character and correlations with electron traps in GaNAs are not obvious especially that the knowledge about point defects in GaNAs is rather limited. In order to attribute the observed PL bands to particular electron traps existing in GaNAs layers, systematic DLTS and LTDLS measurements have been performed for the four samples.

For DLTS and LTDLS study, the epitaxial layers were processed into circular mesas of various diameters ranging from 0.25 to 1 mm using photolithography and wet chemical etching techniques. Ge/Au/Ni/Au were first evaporated and alloyed to form Ohmic contacts to the back of the n^+ GaAs substrate. Schottky contacts were then formed by evaporation of Ti/Au on top of the doped epilayer. Current-voltage (I-V) measurements were carried out to select diodes with the lowest leakage current ($\sim 1 \mu\text{A}$ at -4 V) for the DLTS measurements. Room temperature capacitance-voltage (C-V) characteristics were measured in order to determine the background doping concentration and built-in voltage, which are required for the analysis of the DLTS data. Mott-Schottky plots of the C-V data have been used to determine the electron concentrations. A linear best-fit through the data points shows a uniform doping density over the bias range of -4 V to 0 V used for DLTS and LTDLS measurements. At room temperature, all structures have shown the free carrier concentration of about $4 \times 10^{16} \text{ cm}^{-3}$.

Figure 2 shows the DLTS data obtained for the four GaNAs layers of different nitrogen concentrations and the reference GaAs layer. As illustrated in Fig. 3, DLTS scans reveal the presence of seven (A1 to A7), four (B1 to B4), four (C1 to C4), and three (D1 to D3) electron emitting levels in GaNAs layers with 0.2%, 0.4%, 0.8%, and 1.2% N content, respectively. It is clearly visible that these electron traps are not observed in the reference sample [see Fig. 2(a)] and, therefore, they are attributed to nitrogen incorporation into GaAs host. For a better resolution of electron traps in GaNAs layers, LTDLS measurements were also performed. The DLTS and LTDLS data were analyzed within the standard approach.⁷ The activation energies and apparent capture cross-sections of each trap are calculated from the slope and intercept of Arrhenius plots shown in Fig. 3. The concentration of each trap is obtained from the DLTS peak height and the doping concentration obtained from C-V measurements. The activation energies of electron traps and their cross sections and concentrations have been previously reported in Ref. 10.

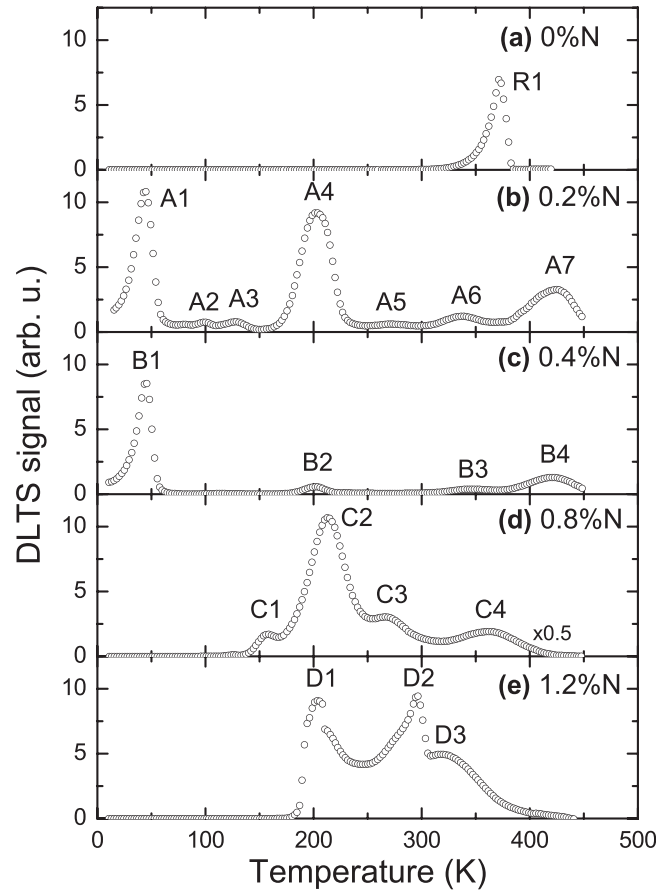


FIG. 2. Standard DLTS spectra of n -type $\text{GaN}_x\text{As}_{1-x}$ layers of various nitrogen concentrations obtained with a reverse bias of -4 V , filling pulse duration of 1 ms , pulse height of -0.5 V , and a sampling rate window of 50 s^{-1} .

As the parameters of electron traps in GaNAs vary significantly with varying nitrogen concentration, it is rather difficult to identify the same traps for all the four samples. On the other hand, it can be also concluded that although the present results are quite similar to previously published data on electron traps in GaNAs,^{8,9,11} it is difficult to make specific trap assignments because the activation energies are strongly dependent on the N content and may vary with the

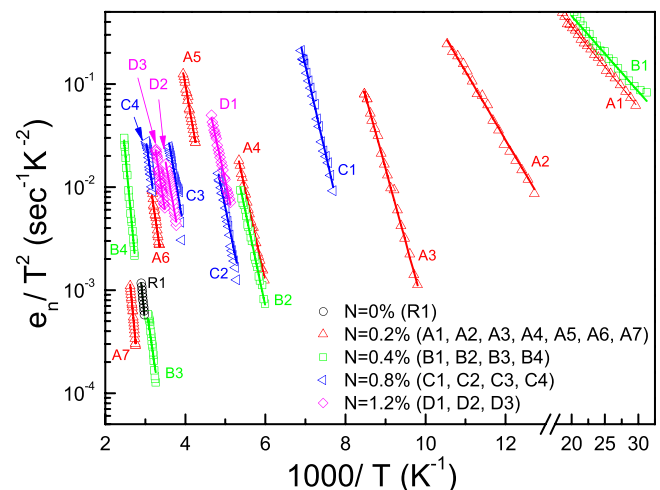


FIG. 3. Arrhenius plots obtained from LTDLS measurements of the thermal emission rates. The determined parameters for electron traps can be found in Ref. 10.

sample quality and preparation methods. An advantage of our approach is that we minimize these effects by using set of samples grown, processed, and measured under similar conditions. In order to establish a correlation between defect traps in different samples, we note that according to the BAC model, the reduction of the band gap with increasing N content originates from downward shift of the conduction band edge with the energy of the valence band edge remaining constant for various N concentrations. For GaNAs alloys with low nitrogen concentration, it can be also assumed that the energy of the same defect is constant relative to the valence band edge. This assumption is illustrated in Fig. 4 and widely commented in the figure caption.

Figure 5 shows positions of the conduction band (CB) minimum and the valence band (VB) maximum for GaNAs plotted as a function of nitrogen concentration. In this plot, it is assumed after the BAC model² that the whole band gap reduction, which is related to the incorporation of N atoms, appears in the conduction band. Energy positions of electron traps measured by the activation energies relative to the CB edge are also drawn in this figure (see open diamonds in Fig. 5). Such a diagram allows us to compare activation energies of electron traps in GaNAs layers with different nitrogen concentrations. From the arguments of constancy of the deep trap energy levels relative to the valence band edge is that deep donor traps (DTs) of the same microscopic nature should be located near a horizontal dashed line in the diagram in Fig. 5, i.e., the activation energy of a given electron

Activation energy for a deep donor trap of the same microscopic nature in GaNAs of various nitrogen concentrations

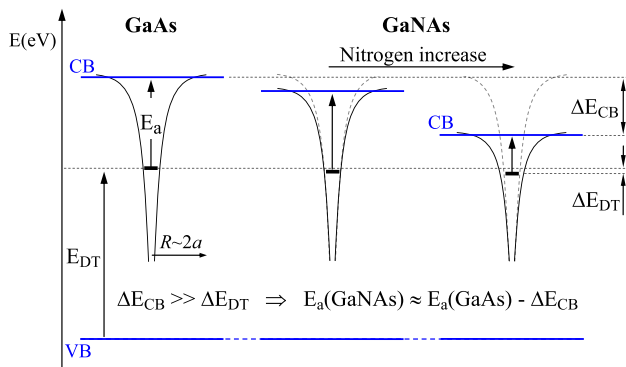


FIG. 4. Sketch of N-related changes in the position of conduction band (ΔE_{CB}), the energy of deep donor trap (E_{DT}), and the activation energy (E_a) for this trap in GaNAs alloys. The deep donor trap is described by a short range potential $V(r)$ (R is the order of 1-2 lattice constants a , i.e., 2-4 nearest-neighbor environments for the point imperfection which is the source of deep donor trap). Because of the short range character of $V(r)$ potential, it can be assumed that the energy of deep donor traps of the same microscopic nature almost does not change relative to the valence band edge with the incorporation of a small amount of nitrogen atoms into GaAs host, i.e., this change (ΔE_{DT}) is much smaller than the N-related shift of the conduction band. Therefore, the activation energy for deep donor trap of the same nature should decrease with the increase in nitrogen concentration according to relation: $E_a(\text{GaNAs}) \approx E_a(\text{GaAs}) - \Delta E_{CB}$. The average distance between nitrogen atoms in GaNAs alloys with $N < 1.25\%$ is much larger than the scale of localizing potential $V(r)$. It is at least 9 nearest-neighbor environments between N atoms versus 2-4 environments for the short range potential $V(r)$. It means that most of GaAs-like deep donor traps in GaNAs alloy have purely GaAs-like environment but their activation energies cannot be the same as in GaAs host since N atoms shift the conduction band towards the deep donor trap E_{DT} as shown in the sketch.

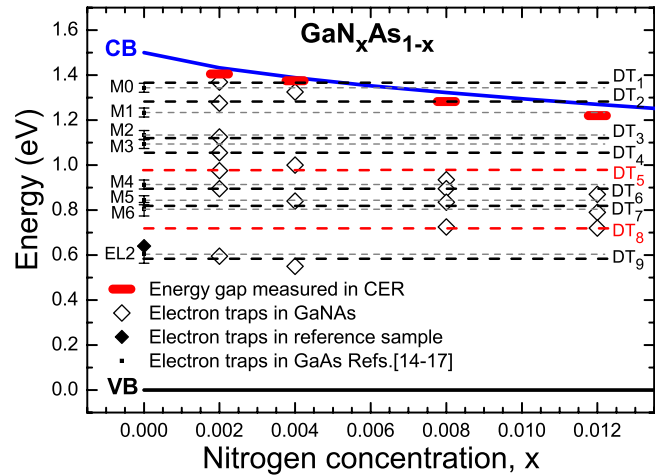


FIG. 5. GaNAs band diagram plotted together with activation energies of electron traps (open diamonds for GaNAs layers and a solid diamond for the reference sample) obtained from LTDLs measurements. Horizontal dashed lines represent GaAs-like (black color) and N-containing (red color) electron traps in GaNAs. Electron traps in GaAs grown by molecular beam epitaxy¹⁴⁻¹⁷ are plotted by solid squares and the estimation of their positions in GaNAs is shown by horizontal dashed grey lines.

trap should decrease with the increase in nitrogen concentration the same as the conduction band. In the four studied GaNAs layers of various nitrogen concentrations, we have found traps with eighteen different activation energies which can be attributed to nine DTs in GaNAs [see horizontal dashed lines marked by DT_i ($i = 1, 9$)]. The microscopic origin of these nine DTs is different. One of them, DT_9 was observed in the reference GaAs sample and therefore is not associated with the N incorporation. The remaining eight traps were not observed in the reference sample (i.e., GaAs) and, therefore, they can be associated either directly or indirectly with the incorporation of N atoms. To clarify the relationship between the electron traps in GaNAs layers and previously identified electron traps in GaAs grown by MBE,¹⁴⁻¹⁷ the known GaAs traps have been plotted in Fig. 5 by solid squares. The horizontal dashed grey lines in Fig. 5 estimate positions of GaAs-like electron traps in GaNAs. It is clear that seven DTs (DT_1 , DT_2 , DT_3 , DT_4 , DT_6 , DT_7 , and DT_9) can be attributed to well known electron traps in GaAs (i.e., M0, M1, M2, M3, M4, M5/M6, and EL2). This suggests that N is not directly involved in these traps but may lead to their formation indirectly by affecting the quality of the GaNAs film. The only two traps that are not observed in GaAs and must involve N atoms are DT_5 and DT_8 . The DT_5 is observed for GaNAs layers with $N \leq 0.8\%$, whereas the DT_8 is observed for samples with $N \geq 0.8\%$. Moreover, it is clearly seen in Fig. 5 that the traps DT_3 , DT_4 , and DT_9 are not observed in GaNAs layers with larger nitrogen concentration. Also the DT_6 trap is not observed for sample with 0.4% N, while this trap is detected for three remaining GaNAs samples. This, tentatively, can be attributed to a change in the defect formation energy associated with the downward shift of the conduction band edge and the Fermi energy with increasing N content. The fact that the DT_6 trap is not observed for the sample with 0.4% N can be attributed to its lower concentration which may result from small variations in the growth conditions for this sample. Although the

actual microscopic nature of the two N-related defects (DT_5 and DT_8) is not known at present, it could be argued that they can be attributed to clusters involving several atoms. It has been shown before that energy of such clusters depends on the number of the N atoms involved with deeper defects containing larger number of N-atoms.^{18,19} Therefore, the concentration of the deeper trap, DT_8 , is higher in samples with larger N content.

Finally, it is worth noting that our assumption on constancy of the deep trap energy levels relative to the valence band edge is weaker for GaNAs alloys with larger nitrogen concentrations since the probability of appearance of nitrogen atoms in the nearest-neighbor environment of point imperfection, which is the source of deep trap, rises with nitrogen concentration. However, in the range of nitrogen concentration $N < 1.25\%$, the assumption that $\Delta E_{CB} \gg \Delta E_{DT}$ is valid and therefore the activation energy of GaAs-like traps in GaNAs can be expressed at the first approximation as $E_a(\text{GaNAs}) \approx E_a(\text{GaAs}) - \Delta E_{CB}$. Some scattering of experimental points around horizontal lines in Fig. 5 is smaller than the N-related shift of the conduction band and can be attributed to ΔE_{DT} , which is neglected in our analysis.

It is expected that DTs participate in emission at low temperatures. The most likely mechanism of this emission is recombination of an exciton trapped by a DT. The electron-hole attraction in GaNAs is large enough to localize a hole around the DT at low temperature and, therefore, the photo-generated carriers can recombine radiatively through DTs at low temperatures. It is a donor trap–valence band (DT-VB) transition with the electron-hole interaction. However, the emission disappears at higher temperatures when the thermal energy is high enough to break the bound exciton. It is also worth noting that the gradual red-shift of the broad emission band well correlates with the overall shift of the DT energies relative to the VB shown in Fig. 5. Moreover, it is worth noting that DTs also participate in recombination processes at room temperature. However, it is non-radiative recombination since the thermal energy at room temperature is larger than the attraction energy between electrons and holes, and hence the electron-hole correlation is loose and, therefore, carriers recombine non-radiatively. This means that GaNAs alloys exhibit poor efficiency of PL at room temperature due to DTs, whose presence is confirmed in our samples by DLTS/LTDLS measurements.

In addition to DT-VB emission, the NB emission is observed few tens meV below the energy gap for samples with larger nitrogen content (see PL spectra for samples with

0.8% and 1.2% N). Such an emission is often observed for Ga(In)NAs layers³ and is attributed to recombination of excitons localized on alloy content fluctuations and/or donor (acceptor) like states.^{4–6}

In conclusion, a simple band gap diagram has been proposed to correlate the activation energies of electron traps measured in DLTS/LTDLS in samples with different N content. The diagram allowed identification of two electron traps associated with nitrogen atoms. A broad PL band well correlates with the location of deep traps.

The authors acknowledge support from the MNiSzW (Grant No. N202 258339), the U.S. Department of Energy, and the COST Action MP0805 focused on study of dilute-nitrides. In addition, R.K. acknowledges for the support within the grant “Mobilnosc Plus” from the MNiSzW.

¹M. Henini, *Dilute Nitride Semiconductors* (Elsevier Ltd., Oxford, 2005) and references therein.

²W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.* **82**, 1221 (1999).

³R. Kudrawiec, G. Sek, J. Misiewicz, L. H. Li, and J. C. Harmand, *Eur. Phys. J.: Appl. Phys.* **27**, 313 (2004).

⁴A. M. Mintairov, K. Sun, J. L. Merz, H. Yuen, S. Bank, M. Wistey, J. S. Harris, G. Peake, A. Egorov, V. Ustinov, R. Kudrawiec, and J. Misiewicz, *Semicond. Sci. Technol.* **24**, 075013 (2009).

⁵R. Kudrawiec, G. Sek, J. Misiewicz, F. Ishikawa, A. Trampert, and K. H. Ploog, *Appl. Phys. Lett.* **94**, 011907 (2009).

⁶M. Latkowska, R. Kudrawiec, G. Sek, J. Misiewicz, J. Ibáñez, M. Henini, and M. Hopkinson, *Appl. Phys. Lett.* **98**, 131903 (2011).

⁷L. Dobaczewski, A. R. Peaker, and K. B. Nielsen, *J. Appl. Phys.* **96**, 4689 (2004).

⁸S. Tanaka, A. Moto, M. Takahashi, T. Tanabe, and S. Takagishi, *J. Cryst. Growth* **221**, 467 (2000).

⁹A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, A. E. Botchkarev, N. N. Nelson, M. M. E. Fahmi, J. A. Griffin, A. Khan, S. N. Mohammad, D. K. Johnstone, V. T. Bublik, K. D. Chsherbachev, M. I. Voronova, and V. S. Kasatochkin, *Solid-State Electron.* **46**, 2155 (2002).

¹⁰M. Shafi, R. H. Mari, M. Henini, D. Taylor, and M. Hopkinson, *Phys. Status Solidi C* **6**, 2652 (2009).

¹¹B. Bouzazi, K. Nishimura, H. Suzuki, N. Kojima, Y. Ohshita, and M. Yamaguchi, *Curr. Appl. Phys.* **10**, S188 (2010).

¹²R. Kudrawiec, *Phys. Status Solidi B* **247**, 1616 (2010).

¹³I. Vurgaftman and J. R. Meyer, *J. Appl. Phys.* **94**, 3675 (2003).

¹⁴D. V. Lang, A. Y. Cho, A. C. Gossard, M. Illegems, and W. Wiegmann, *J. Appl. Phys.* **47**, 2558 (1976).

¹⁵R. Y. DeJule, M. A. Haase, G. E. Stillman, S. C. Palmateer, and J. C. M. Hwang, *J. Appl. Phys.* **57**, 5287 (1985).

¹⁶Y.-C. Pao, D. Liu, W. S. Lee, and J. S. Harris, *Appl. Phys. Lett.* **48**, 1291 (1986).

¹⁷A. Kitagawa, A. Usami, T. Wada, Y. Tokuda, and H. Kano, *J. Appl. Phys.* **65**, 606 (1989).

¹⁸P. R. C. Kent and A. Zunger, *Appl. Phys. Lett.* **82**, 559 (2003).

¹⁹A. Lindsay and E. P. O'Reilly, *Phys. Rev. Lett.* **93**, 196402 (2004).