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Strong surface passivation of GaAs nanowires with ultrathin InP and GaP capping layers

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We demonstrate efficient surface passivation of GaAs nanowires using ultrathin *in-situ* grown epitaxial InP and GaP capping layers, with metallo-organic vapor phase epitaxy as the growth system. The passivation increased photoluminescence intensity by three orders of magnitude compared to unpassivated nanowires, and the effect remained strong after a month of storage in air. Effective passivation was acquired over a wide range of growth temperatures, although the highest studied temperatures caused additional detrimental effects such as etching and GaAsP formation. The capping layer thickness was in the order of few monolayers. Therefore, the impact on any other properties of the nanowires besides the surface states was minuscule. As a simple and effective method the studied capping layers offer an excellent way for nanowire passivation. © *2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4891535]

Semiconductor nanowires (NWs) provide a promising path to produce numerous nanoscale devices, such as light-emitting diodes,[1] solar cells,[2] and transistors.[3] For many of these devices, however, surface states can be detrimental due to Fermi level pinning and depletion of charge carriers. A depletion layer caused by the surface states can extend through the whole nanowire diameter,[4,5] thus rendering them unusable for device structures. Moreover, the surface states can further reduce conductivity by scattering the charge carriers.[6] These effects are pronounced in GaAs due to its high surface recombination rate. GaAs is otherwise a widely used material with its several desired properties, such as high electron mobility and a direct band gap with suitable energy to single-junction solar cells. Therefore, passivation of the GaAs surface is vital and has therefore been under intensive research in the past years. The most widely used GaAs nanowire surface passivation methods utilize closely lattice-matched shells of a different material. The reported shell materials include most commonly used AlGaAs,[5,7–9] AlInP,[10] and InGaP.[11] However, a thick shell with a different band gap inevitably affects the band structure and nanowire morphology, thus limiting further processing possibilities. Moreover, lattice-matching requires careful tuning of growth parameters for each individual system which is often tedious in 3D nanowire growth (except with AlGaAs). The shell growth can be avoided by passivating the surface with sulfur, but that method has been reported to suffer from stability issues.[12]

We report here an alternative, simple passivation method for GaAs nanowires based on an *in-situ* grown ultrathin InP or GaP capping layer. We show that already a few-monolayer (ML) thick capping layer provides efficient passivation without need to grow shells with a thickness of several nanometers. These few-monolayer thick layers require no lattice-matching and they have little impact on the nanowire morphology or the band structure. This method has been previously used on near-surface quantum wells with enhancements of photoluminescence (PL) intensity up to four orders of magnitude and with good stability.[13–15] The passivation in this method results primarily from reduced surface recombination velocity,[16] which is over three orders of magnitude faster in GaAs NWs than in InP NWs.[6] We show that this technique is suitable for GaAs nanowires as well, with enhancements in PL reaching three orders of magnitude and with good stability.

The GaAs NWs were fabricated using an atmospheric pressure metallo-organic vapor phase epitaxy reactor with trimethylgallium (TMGa), trimethylindium (TMIn), trimethylaluminum (TMAl), tertiarybutylarsine (TBAs), and tertiarybutylphosphine (TBP) as precursors for Ga, In, Al, As, and P, respectively. The NW growth was initiated by introducing TMGa (10.8 μmol/min) and TBAs (270 μmol/min) simultaneously to the reactor after heating the sample to the growth temperature of 430 °C. The relatively low growth temperature was chosen to avoid tapering and to minimize any effects arising from varying diameter. The NW growth step was 300 s long after which the TBAs flow was switched off and TBP on (flow rate 880 μmol/min). The reactor temperature was then raised to the passivation temperature which ranged from 470 °C to 650 °C. At this temperature, 5 μmol/min of either TMIn or TMGa was introduced to the reactor in order to grow an InP or a GaP capping layer, respectively. Additionally, passivation with surface phosphidization was studied by omitting the group III flow during this step. Phosphidization occurred during heating to the passivation temperature and subsequent cooling. Based on previously reported values, phosphidization is expected to form approximately 1–2 monolayers of GaP on the surface of GaAs.[17] For thin films, the used TBP and TMIn flows result in nominally 1 ML of InP at 650 °C in 0.63 s in the used system. In case of NWs, the material is distributed to a

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larger surface area and therefore the resulting layer is thinner, and lower deposition temperature further reduces the growth rate. Therefore, the capping layer growth rate is estimated as ~1 ML per second for the passivation temperatures of 600 °C–650 °C and less for lower temperatures. After the capping layer deposition, the TBP flow was kept open during cooling down to 270 °C. In addition, GaAs/AlGaAs core-shell NWs were grown in order to compare the passivation efficiency to a more widely used method. These NWs were passivated with an AlGaAs shell by keeping the TBAs flow open after the core growth and growing the shell by adding TMAl and TMGa to the reactor for 20 s at 650 °C. The used substrates were Si(111) that were cleaned with acetone, isopropanol, and deionized water prior to the growth. Au nanoparticles with 40 nm diameter were dispersed onto the substrates from a colloidal solution using poly-L-lysine to enhance adhesion.

Characterization methods included scanning electron microscopy (SEM) (Zeiss Supra 40), transmission electron microscopy (TEM) (JEOL JEM-2200FS operated at 200 kV), energy-dispersive X-ray spectroscopy (EDX) integrated in the TEM. TEM was used in bright field, high-angle annular dark-field (HAADF), and scanning TEM (STEM) modes. The TEM samples were prepared by placing a holey carbon grid on a NW sample and applying mechanical force in order to break the NWs and to attach them to the carbon grid. In addition, the NWs were studied with PL measurements, in which the NWs were excited using a continuous wave laser with 532 nm wavelength, a spot size of ~100 μm and excitation power of ~40 mW. The signal was detected using a lock-in amplifier, a monochromator, and a liquid nitrogen cooled germanium p-i-n detector. For low temperature (LT) measurements, the samples were cooled using a closed cycle helium cryostat. The PL measurements were performed 1–2 days after the growth.

Passivation enhanced the PL intensity markedly at all of the tested passivation temperatures. Fig. 1 shows the PL spectra measured at 12 K from nanowires passivated at 470 °C–650 °C with InP for 3 s. Moderate passivation temperatures of 470 °C–550 °C resulted in a clear PL peak at approximately 820 nm (1.51 eV), which corresponds well to the band-to-band transition of GaAs. For these NWs, typical full width at half maximum values of the PL peaks were 35–40 meV, which are comparable to previously reported values for GaAs NWs.[7,18] However, in contrast to the passivated NWs, no PL signal was detected from the unpassivated nanowires even at low temperature. The LT PL intensity from the passivated nanowires was three orders of magnitude higher than the lowest measurable signal in our system. Since no signal was acquired from the unpassivated nanowires, the enhancement in PL intensity was at least three orders of magnitude. This enhancement is very high compared to most of the earlier reported GaAs NW passivation efficiencies.[5,8,10]

In addition to the GaAs-related peak, a clear tail emerges at longer wavelengths with passivation temperatures of 550 °C–600 °C. This low-energy tail is attributed to the InP capping layer, which is thicker (and thus contributes more to the signal) at higher temperatures due to more efficient precursor cracking and layer growth. Interestingly,
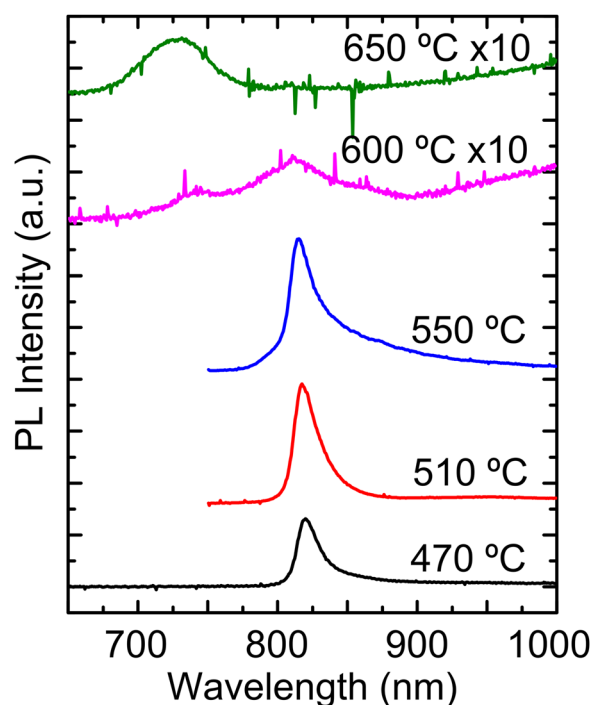

FIG. 1. Low-temperature PL spectra measured from GaAs NWs passivated with InP for 3 s at 470 °C–650 °C.

when the passivation temperature was increased to 600 °C or above, the PL intensity decreased by roughly an order of magnitude. At these elevated temperatures, another peak emerged at a higher energy of ~1.7 eV (730 nm wavelength). In fact, at 650 °C only this high-energy peak was observed, and no transition corresponding to the GaAs band gap. The high-energy peak is expected to originate from GaAsP that formed at elevated temperatures in phosphorus-rich environment. The composition was roughly $GaAs_{0.82}P_{0.18}$ as calculated from Vegard's law with a bowing parameter of 0.19 (Ref. 19). The phosphorus-rich environment was additionally found to etch the NW surface, which results in roughness, increased number of surface states and a decreased PL intensity. Since the only observed transitions were related to GaAsP at 650 °C, we suspect that phosphorus diffused through the whole nanowire diameter. The broadness of the spectra is attributed to varying GaAsP composition along the diameter. Both GaAsP formation and NW etching were observed in TEM studies as shown later in this Letter.

Fig. 2 shows SEM and TEM micrographs from NWs passivated at different temperatures with different InP capping times and with phosphidization. Nearly pristine nanowires after passivation at 470 °C with InP for 3 s are shown in Figs. 2(a) and 2(b). The SEM characterization revealed randomly oriented NWs with an approximated length of 10 μm (Fig. 2(a)). SEM images taken from different samples appeared nearly identical indicating a good repeatability of the growth process. TEM images taken from the NWs passivated with InP at 470 °C for 3 s showed no observable effects on the nanowire crystal structure (Fig. 2(b)), which was zincblende (see diffraction pattern in the inset) with few twin planes. The only observable effect resulting from the passivation was a faint phosphorus peak in EDX when measured at the nanowire edge. On the other hand, when the
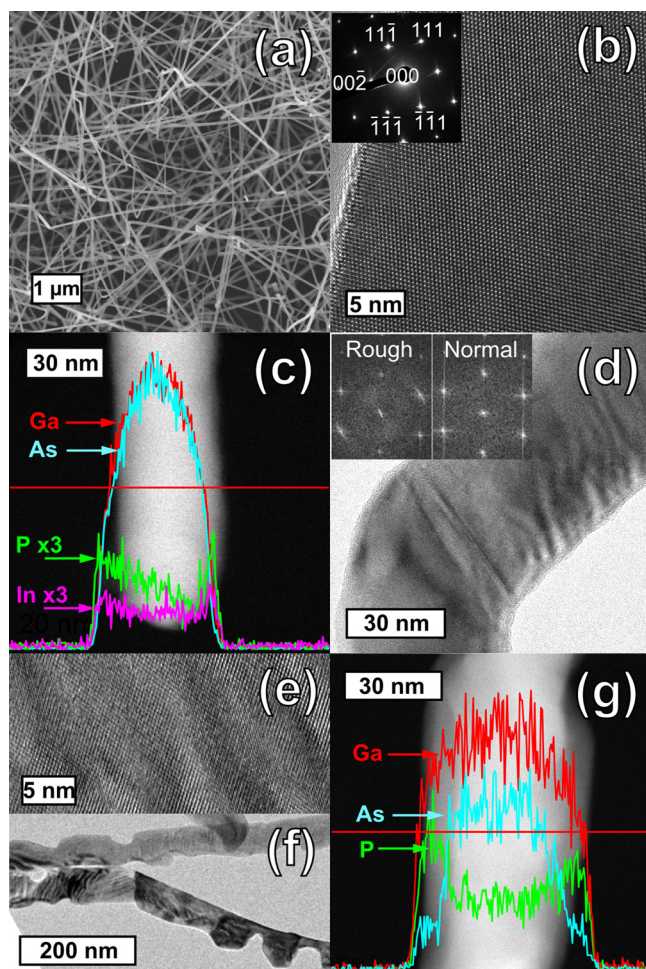
FIG. 2. SEM (a) and TEM ((b)–(g)) micrographs from nanowires passivated with InP at 470 °C for 3 s ((a) and (b)), with InP for 10 s at 550 °C (c), with InP for 5 s at 600 °C (d), and with phosphidization at 650 °C ((e)–(g)). TEM HAADF and STEM modes and EDX linescans were used in (c) and (g). Inset in (b) shows a diffraction pattern from the same NW as presented in (b). Inset in (d) shows FFT patterns from a clear and a rough area from the same NW as presented in (d). The red lines in (c) and (g) indicate the EDX measurement line.

650 °C, etching of the GaAs crystal became distinct. Figs. 2(e) and 2(f) show TEM images of nanowires passivated at 650 °C using phosphidization. Large sections of the NWs are etched and the surface roughness is clearly visible. The formation of GaAsP at this temperature was apparent in the PL measurements and is supported by the EDX analysis shown in Fig. 2(g). These results show that not only As-P exchange was taking place at the surface but also phosphorus diffusion and gas-phase etching.

Capping layer deposition time, i.e., thickness, was studied in addition to the passivation temperature. Fig. 3 presents PL spectra measured from nanowires passivated at 470 °C with different capping layer deposition times (i.e., the time that TMIn flow is open). With the capping time of 1 s, the peak is sharp and only a weak tail is visible on the low-energy side. Above the capping time of 3 s, the GaAs band-to-band transition weakened somewhat and the low-energy signal became more apparent until it finally dominated with the capping time of 7.5–10 s. This low-energy signal is attributed to the InP capping layer, which emits a blueshifted signal compared to InP band gap (873 nm) under compressive strain due to the 3.8% lattice mismatch between GaAs and InP.[16] The blueshift is weakest with the thickest layers, which is assumed to result from dislocation formation, e.g., at defect locations and following strain relaxation. The formation of the dislocations additionally agrees with the weakening of the GaAs-related signal, since dislocations in the passivating InP layer have been observed to decrease the PL intensity.[16] Another possible cause for the varying peak position of the InP-related signal is quantization, which weakens as the layer becomes thicker. The broadness of the low-energy signal stems from varying thickness in the capping layer due to the shadowing effect in the relatively long NW forest. It is also noteworthy that no InP segment was

passivation temperature was raised to 550 °C and the capping time to 10 s, the passivating InP layer was clearly apparent in EDX as shown in Fig. 2(c). However, the EDX signals from In and P were very weak compared to Ga and As, suggesting that the passivating layer remained very thin also with a relatively high temperature and a long capping time. Since the studied capping layers were extremely thin, they pose little impact on the structural or electrical properties of the nanowires besides those resulting from surface passivation.

A nanowire passivated at 600 °C with InP for 5 s is shown in Fig. 2(d). There are clear contrast differences visible on the nanowire surface. These contrast differences suggest that the surface has become rough during the passivation, which we attribute to As-P exchange and etching of GaAs by phosphorus. Additionally, fast Fourier transformation (FFT) pattern taken on the modified surface showed a distorted diffraction pattern, which indicates the material no longer comprised single crystal (see comparison between normal and rough areas in the inset). Nevertheless, approximately half of the nanowires were free of such surface roughness. As the passivation temperature was increased to
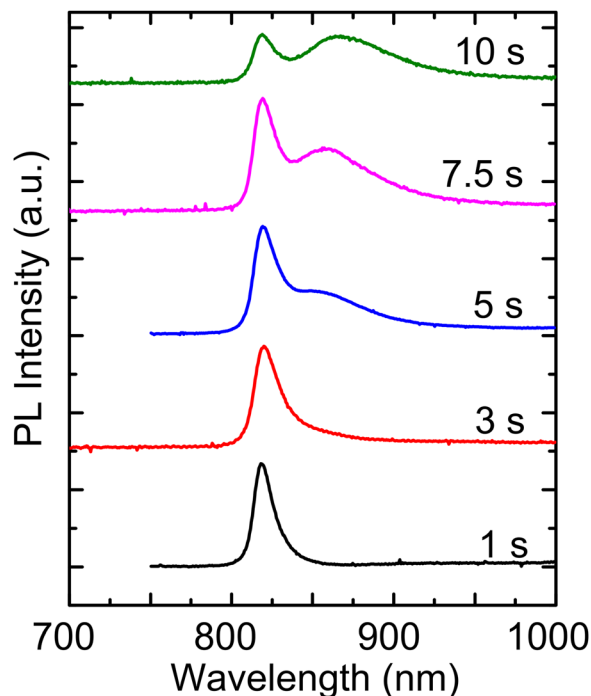

FIG. 3. Low-temperature PL spectra measured from GaAs NWs passivated with InP for 1–10 s at 470 °C.

seen growing under the Au seed in TEM and EDX measurements, and therefore the only possible origin of the InP signal is the capping layer.

Finally, Fig. 4 presents PL intensities measured from samples passivated at 470 °C–650 °C with phosphidization, InP capping, and GaP capping. The highest intensities were acquired with the InP passivation time of ∼3 s at 470 °C–550 °C. However, the difference was relatively small with only a factor of 2 separating the highest and the lowest intensities. More importantly, the thicker InP capping layer provided no benefits, but instead weakened the GaAs-related PL intensity and formed dislocations. In order to avoid this, the InP capping time should be kept below 5 s. On the other hand, short InP passivation showed better stability compared to passivation with phosphidization, which was apparent in PL intensities measured after a month of storing in ambient air (see Fig. 4(b)). The intensities dropped by approximately 30% in the InP passivated samples and more dramatically

when phosphidization was used. The PL intensity has been observed to drop faster with phosphidization in earlier research as well.[15] Therefore, 1–3 s InP passivation is optimal for the best enhancement in PL and for a stable passivation, while phosphidization suffices when no long term stability is required. Regarding the passivation temperature, 470 °C–550 °C provided the strongest passivation effect, whereas the PL intensity dropped at 600 °C–650 °C. Since the temperatures 470 °C–550 °C and different passivation times resulted in nearly equally strong passivation, we conclude the method to be quite insensitive to changes in growth parameters.

In addition to the passivations with InP and phosphidization, GaP capping layers were studied. The PL intensities were comparable to those acquired with InP although somewhat lower (Fig. 4(a)). GaP passivation is therefore a viable alternative to InP. Additionally, GaAs/AlGaAs core-shell structures were fabricated in order to compare the acquired intensities to a more widely used method. Regardless the relatively thick AlGaAs shell, the measured PL intensity was slightly lower compared to the InP passivation at 470 °C–550 °C with a factor of 2–3 separating the peak intensities. Moreover, the PL peak was broader and the peak position was redshifted (the redshift is discussed elsewhere[9]). For these reasons, and due to the required high deposition temperature and the additional effects the thick shells pose on the NW structure, the ultrathin capping layers could be a superior choice as a passivation method in many cases.

In conclusion, GaAs nanowires were passivated using ultrathin InP and GaP capping layers. The enhancement in PL intensity was at least three orders of magnitude as compared to unpassivated NWs, and the passivation was successful over a wide range of parameters. However, high temperatures were observed to cause formation of GaAsP and NW etching, and a long capping time provided no benefits but weakened the PL intensity from the GaAs NWs. The InP passivation was additionally stable which was seen as just a ∼30% drop in PL intensity after one-month storage in ambient air. Furthermore, the passivation efficiency with the ultrathin capping layers was similar or slightly stronger compared to the widely used GaAs/AlGaAs core-shell structures. The results suggested an optimal temperature range of 470 °C–550 °C and a InP capping time of 1–3 s. Passivation with GaP layers was slightly weaker compared to InP. Additionally, extremely simple passivation with phosphidization provided a strong PL signal, although with poorer stability, and is therefore a viable alternative when no long term stability is needed. We believe that numerous GaAs nanowire applications can benefit from the efficiency and the simplicity of the reported method.
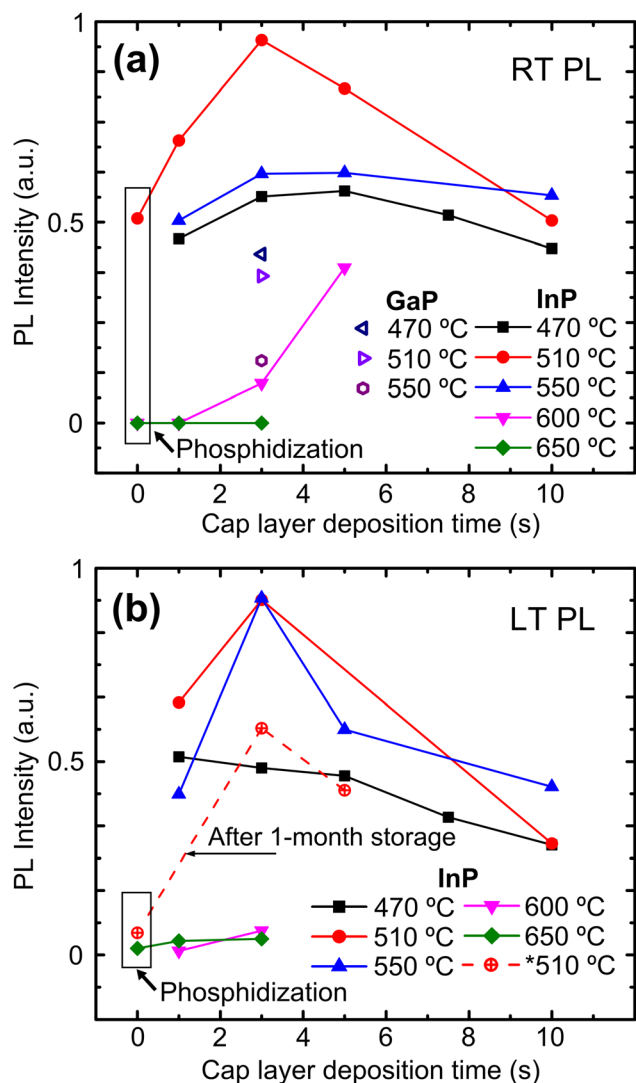

FIG. 4. PL intensities measured at room temperature (RT) (a) and at 12 K (b) from NWs passivated at 470–650 °C with InP or GaP for 1–10 s and with phosphidization (denoted with 0 s cap layer deposition time). InP is denoted with solid symbols and GaP with hollow symbols. In (b) * denotes intensities measured after a month of storage. The data points present averaged intensities from 2 to 3 spots within a sample and from 1 to 2 samples. The connecting lines serve as guides for the eye.

[1]F. Qian, S. Gradecak, Y. Li, C.-Y. Wen, and C. M. Lieber, Nano Lett. **5**, 2287 (2005).

[2]J. Wallentin, N. Anttu, D. Asoli, M. Huffman, I. Åberg, M. H. Magnusson, G. Siefer, P. Fuss-Kailuweit, F. Dimroth, B. Witzigmann, H. Q. Xu, L. Samuelson, K. Deppert, and M. T. Borgström, Science **339**, 1057 (2013).

[3]J. Goldberger, A. I. Hochbaum, R. Fan, and P. Yang, Nano Lett. **6**, 973 (2006).

[4]O. Demichel, M. Heiss, J. Bleuse, H. Mariette, and I. A. F. Morral, Appl. Phys. Lett. **97**, 201907 (2010).

[5]C.-C. Chang, C.-Y. Chi, M. Yao, N. Huang, C.-C. Chen, J. Theiss, A. W. Bushmaker, S. Lalumondiere, T.-W. Yeh, M. L. Povinelli, C. Zhou, P. D. Dapkus, and S. B. Cronin, Nano Lett. **12**, 4484 (2012).

[6]H. J. Joyce, C. J. Docherty, Q. Gao, H. H. Tan, C. Jagadish, J. Lloyd-Hughes, L. M. Herz, and M. B. Johnston, Nanotechnology **24**, 214006 (2013).

[7]T. B. Hoang, L. V. Titova, J. M. Yarrison-Rice, H. E. Jackson, A. O. Govorov, Y. Kim, H. J. Joyce, H. H. Tan, C. Jagadish, and L. M. Smith, Nano Lett. **7**, 588 (2007).

[8]L. V. Titova, T. B. Hoang, H. E. Jackson, L. M. Smith, J. M. Yarrison-Rice, Y. Kim, H. J. Joyce, H. H. Tan, and C. Jagadish, Appl. Phys. Lett. **89**, 173126 (2006).

[9]V. Dhaka, J. Oksanen, H. Jiang, T. Haggren, A. Nykänen, R. Sanatinia, J.-P. Kakko, T. Huhtio, M. Mattila, J. Ruokolainen, S. Anand, E. Kauppinen, and H. Lipsanen, Nano Lett. **13**, 3581 (2013).

[10]A. C. E. Chia, M. Tirado, Y. Li, S. Zhao, Z. Mi, D. Comedi, and R. R. Lapierre, J. Appl. Phys. **111**, 094319 (2012).

[11]N. Sköld, L. S. Karlsson, M. W. Larsson, M.-E. Pistol, W. Seifert, J. Trägårdh, and L. Samuelson, Nano Lett. **5**, 1943 (2005).

[12]N. Tajik, Z. Peng, P. Kuyanov, and R. R. Lapierre, Nanotechnology **22**, 225402 (2011).

[13]H. Lipsanen, M. Sopanen, M. Taskinen, J. Tulkki, and J. Ahopelto, Appl. Phys. Lett. **68**, 2216 (1996).

[14]A. Aierken, J. Riikonen, J. Sormunen, M. Sopanen, and H. Lipsanen, Appl. Phys. Lett. **88**, 221112 (2006).

[15]A. Aierken, T. Hakkarainen, J. Tiilikainen, M. Mattila, J. Riikonen, M. Sopanen, and H. Lipsanen, J. Cryst. Growth **309**, 18 (2007).

[16]Y. Wada and K. Wada, Appl. Phys. Lett. **63**, 379 (1993).

[17]R. Beaudry, S. P. Watkins, X. Xu, and P. Yeo, J. Appl. Phys. **87**, 7838 (2000).

[18]A. Lysov, M. Offer, C. Gutsche, I. Regolin, S. Topaloglu, M. Geller, W. Prost, and F. J. Tegude, Nanotechnology **22**, 085702 (2011).

[19]S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).