Study on irradiation-induced defects in GaAs/AlGaAs core–shell nanowires via photoluminescence technique

Li-Ying Tan(谭立英), Fa-Jun Li(黎发军)†, Xiao-Long Xie(谢小龙), Yan- Ping Zhou(周彦平), and Jing Ma(马晶)

National Key Laboratory of Tunable Laser Technology, Harbin Institute of Technology, Harbin 150001, *China*

(Received 27 February 2017; revised manuscript received 30 April 2017; published online 20 June 2017)

To gain a physical insight into the radiation effect on nanowires (NWs), the time resolved photoluminescence (TRPL) technique is used to investigate the carrier dynamic behaviors in GaAs/AlGaAs core–shell NWs before and after 1-MeV proton irradiation with fluences ranging from 1.0×10^{12} cm^{-2} to 3.0×10^{13} cm^{-2}. It is found that the degradations of spectral peak intensity and minority carrier lifetime show similar trends against irradiation fluence, which is closely related to the displacement defects induced by irradiation. We also find that the proton irradiation-induced defects behave as Shockley–Read–Hall (SRH) recombination center trapping free carriers. Finally, the defect concentration could be estimated through measuring the minority carrier lifetime.

Keywords: radiation effect, minority carrier lifetime, defect concentration, radiation damage

PACS: 62.23.Hj, 61.72.–y, 61.80.–x, 61.80.Jh **DOI:** 10.1088/1674-1056/26/8/086201

1. Introduction

Recently, due to the excitation of unique electronic and optical properties of these nanostructure, GaAs/AlGaAs core/shell NWs have been studied in a broad range of optoelectronic devices such as light-emitting diodes,[1] laser diodes,[2,3] solar cells,[4,5] and photodetectors[6,7] working towards the energy conservation and environment protection. One important point is that as an alternative material to silicon, GaAs offers the possibility of higher radiation resistance[8] and a better overall performance.[9] However, despite these advances, there is still an uncertainty over the role of point defects and/or defect clusters that may be present at exceedingly high density, which could destroy semiconductor devices in the radiation environment, such as space and atom energy field. The materials used in the relevant units above must withstand long-term use in strong radiation fields. It is well known that nano-material and nano-devices, such as quantum dot[10] and quantum well,[11] present radiation hardness intrinsically.[12–15] Although the proton irradiation-induced intermixing effect in GaAs-AlGAs quantum well has been investigated[16–18] and ultra-thin GaAs solar cell with intrinsic radiation tolerance has been demonstrated,[19] these results have not been comprehensively explained due to the lack of systemized theory and data study. In terms of ion irradiation on NWs, currently the research mainly focuses on the doping profile of NWs,[20,21] or bending and alignment for shaping NWs.[21,22] Therefore, it is significant to develop the radiation effect theory and conduct experiments on NWs to understand the radiation effect on NWs in this corresponding area.

There are two categories of defects created by radiation, and they have distinctively different characteristics.[23] The first category, called point defects, includes at most a few atoms aggregated together to form a relatively stable and simple defect. The second category, called a defect cluster, involves a few hundred atoms in a large disordered region. A displacement damage effect occurs when displacement defects are created in the crystal lattice, thereby introducing additional states in the forbidden band. This displacement damage to optoelectronics devices in the Van Allen belt by electrons and protons tends to be of the simple defect variety.[23] Apparently in this case, the transmission electron microscope (TEM) technique is unable to provide enough resolution to directly observe the point defect in the crystal. Other techniques such as temperature-dependent Hall-effect (TDH), deep-level transient spectroscopy (DLTS), positron annihilation spectroscopy (PAS), and photoluminescence (PL) spectroscopy, have been employed to characterize single crystal and their defect states. While the first three techniques are used for studying materials from different viewpoints, they are the known well-established tool for bulk solids and thin films.[24,25] These methods show several limitations and technical challenges, because of the formation of Ohmic contact for instance. Besides, the displacement lattice damage in semiconductor material can have a significant influence on their electrical or optoelectronic properties, through creating more than one deep-level defect in the bandgap. Consequently, the important material parameters such as free carrier mobility and density, resistivity and generation and recombination lifetime will be affected by displacement damage. The relevant study on single NW is likely to be an extreme challenge, such as the stabil-

†Corresponding author. E-mail: lifajun1201@gmail.com

© 2017 Chinese Physical Society and IOP Publishing Ltd

ity of fabricating a single NW device. On the other hand, micro-photoluminescence spectroscopy (μ-PL) could largely overcome these difficulties. In addition, it can be applied to the case where there is a low defect concentration in single NW, provided that competitive non-radiative carrier recombination is not the overwhelming optical transition. Our previous study has demonstrated that the NWs with smaller diameter, which has a relatively high surface-to-volume ratio, could have greater radiation tolerance.[26] This work highlights the potential of the photoluminescence technique to estimate the irradiation-induced defect concentration by measuring minority carrier lifetime of NWs.

2. Experimental details

All the samples and equipment used in this study were provided by the Semiconductor Optoelectronics and Nanotechnology Group at the Department of Electronic Material Engineering, Australian National University. The GaAs/AlGaAs core-shell NWs grown via the metal-seeded vapor–liquid–solid (VLS) growth method in a metal–organic vapor phase epitaxy (MOVPE) system. The growth of the NWs, structural characterization, and PL characterization methods have been described in earlier publications by Joyce *et al.*[27–29] Trimethylgallium (TMGa), trimethylaluminum (TMAl), and arsine were used as the precursors for Ga, Al, and As, respectively. Gold particle size $\sim$ 50 nm was used and GaAs core NWs were grown using the two-temperature procedure.[30] An AlGaAs shell was then grown around the GaAs core at 750 °C with an Al mole fraction of 0.5 (ratio of TMAl/(TMAl+TMGa)= 0.5) in the vapor phase. The SEM image of the grown GaAs/AlGaAs NWs is shown in Fig. 1(a). After growth, the NWs were randomly dispersed (Fig. 1(b)) onto silicon dioxide on silicon (SiO_2-on-Si) substrates for PL and time-resolved photoluminescence (TRPL) measurements. The PL measurements were performed in conjunction with TRPL spectroscopy: the PLs at the peak emission wavelengths before and after irradiation were measured. A monochromator with a cooled charge coupled device (CCD) (for spectral information) and a single photon counting system (for lifetime data) with an instrument response of $\sim$ 50 ps at full width at half maximum (FWHM) and 20.8-MHz repetition rate pulsed laser were used for measuring PL and TRPL, respectively. The cluster/ensemble of NWs were excited by a 522-nm solid state pulsed laser with a $\sim$ 100-μm diameter focal spot through a 10× objective lens at an average power of $\sim$ 3.57 W/cm^2. More importantly, the measuring platform was mounted in a three-dimensional (3D) stepping motor system with positioning resolution $\sim$ 200 nm, which offers a relatively precise position control. It should be pointed out that the measuring uncertainty of PL intensity was about ±5%, estimated through multiple measurements.

All the samples were irradiated by using 1-MeV H^+ ions at room temperature on a Pelletron® tandem accelerator. To be more specific, further details can be found in Ref. [26]. It should be pointed out that all the samples were not annealed after irradiation. The ion fluences from 1.0×10^{12} cm^{-2} to 3.0×10^{13} cm^{-2}, corresponding to total integrated doses of 570 krad and 17100 krad (Si), respectively.[31]

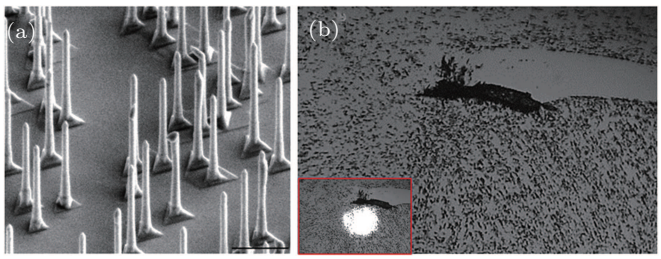


Fig. 1. (color online) (a) Image of the GaAs/AlGaAs core–shell NW with core diameter $\sim$ 50 nm, and AlGaAs shell thickness $\sim$ 30 nm (Scale bar $\sim$ 1 μm). (b) GaAs NWs dispersed as a cluster on SiO_2-on-Si substrate for irradiation. The inset shows the NWs shinning by laser spot.

3. Results and discussion

The plots of the PL intensity as a function of wavelength at different irradiation fluences for a typical cluster of GaAs/AlGaAs core/shell NWs are shown in Fig. 2, which manifests that with increasing fluence the NWs exhibit a decrease of PL intensity. The plots of room-temperature TRPL decay spectra versus irradiation fluence are displayed in Fig. 3, which demonstrates that the TRPL spectra decay faster with fluence increasing. The plots of minority carrier lifetime versus irradiation fluence ($> 10^{12}$ cm^{-2}) are also presented in the inset of Fig. 3. The corresponding minority carrier lifetime is extracted from fitting TRPL spectrum data by mono-exponential decay equation: $I(t) = I_{t=0}\,\mathrm{e}^{-t/\tau}$, where τ is the minority carrier lifetime, $I_{t=0}$ and $I(t)$ are the PL intensities at the moments of 0 and t, respectively.

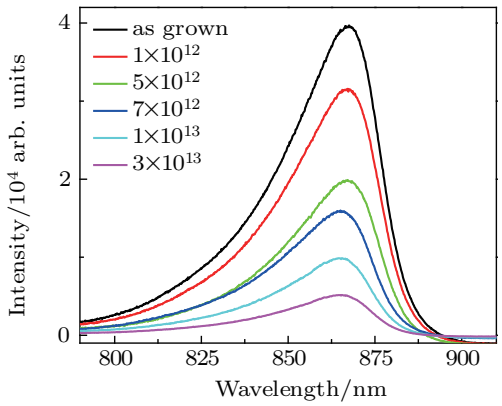


Fig. 2. (color online) Plots of room-temperature PL spectra of GaAs/AlGaAs NWs irradiated at fluences ranging from 1.0×10^{12} cm^{-2} to 3.0×10^{13} cm^{-2}, excited by 522-nm laser. Data for the as-grown samples are also included for reference.

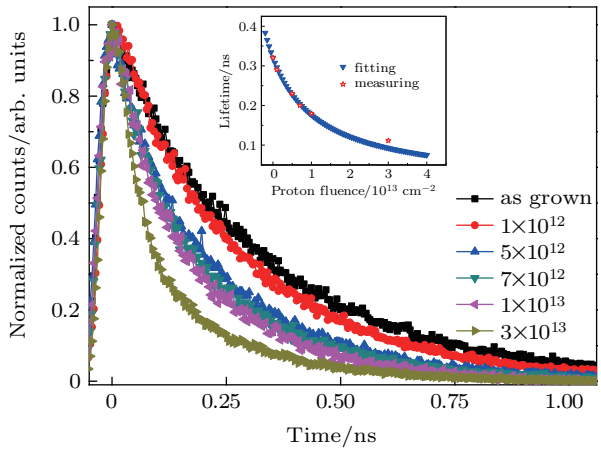


Fig. 3. (color online) Plots of typical photoluminescence decay spectra at room temperature from NWs cluster with irradiation fluences ranging from 1.0×10^{12} cm^{-2} to 3.0×10^{13} cm^{-2}. Data for the as-grown samples are also included for reference. The inset shows the variations of measured minority carrier lifetime with irradiated fluence and fitting results.

Considering the fact that the minority carrier lifetime τ_0 is the reciprocal of the recombination rate R_0 before irradiation, it can be written as $\tau_0 = 1/R_0$. Accordingly, after irradiation the minority carrier lifetime in NW can be given by[23]

$$\tau = 1/R = \frac{1}{R_0+k\varphi}, \tag{1}$$

where R is the post-irradiated recombination rate of the minority carrier in NW, k is the radiation damage constant, and φ is the proton fluence. According to Eq. (1), the data and fitting are plotted and shown in the inset of Fig. 3 (where $\tau_0 = 0.32$ ns).

Then the corresponding carrier lifetime damage coefficient k_τ can be defined as[32–36]

$$k_\tau = \frac{\partial(1/\tau)}{\partial\varphi} \approx \frac{1/\tau(\varphi) - 1/\tau(0)}{\varphi}, \tag{2}$$

where $\tau(\varphi)$ and $\tau(0)$ (here $\tau(0) = \tau_0$) are the post and pre-irradiated lifetime, respectively. The degradation of carrier lifetime τ is the utmost concern on the semiconductor device operation against irradiation.[37]

To directly see the reduction of minority carrier lifetime and degradation of the PL intensity versus radiation fluence, here we define the normalized carrier lifetime as

$$\tau_{\text{Normalized}} = \frac{\tau(\varphi)}{\tau_0} = \frac{1}{1+\tau_0 k_\tau \varphi}, \tag{3}$$

and normalized PL intensity as

$$I_{\text{Normalized}} = \frac{I_{\text{PL}}(\varphi)}{I_0}, \tag{4}$$

$I_{\text{PL}}(\varphi)$ and I_0 are the post and pre-irradiated PL peak intensity, respectively. The normalized PL intensity and carrier lifetime calculated from Eqs. (3) and (4) are plotted in the inset of Fig. 4, revealing that both of them have the same trend as a function of irradiation fluence.

Under low level injection conditions, the dependence of PL intensity on external injection and minority lifetime in NWs can be expressed as:[26]

$$I_{\text{PL}}(\lambda) \propto r^{\text{sp}} U \tau_{\text{mc}}, \tag{5}$$

where r^{sp} is the minority carrier spontaneous radiation rate and U is the external injection. Apparently, equation (5) shows that the normalized PL intensity and normalized lifetime versus fluence have similar trends. Hereby, the linear relationship between carrier lifetime and PL intensity in NWs could be confirmed. Furthermore, for comparing with the normalized carrier lifetime, the PL damage coefficient k_{I} can be defined and the corresponding normalized PL intensity Eq. (4) can be expressed as

$$I_{\text{Normalized}} = \frac{1}{1+I_0 k_I \varphi}. \tag{6}$$

According to Eqs. (6) and (3), the measured normalized PL intensity and carrier lifetime could be fitted and the results are shown in Fig. 4, respectively. The degradation of PL intensity and carrier lifetime reflect both decrease dramatically once the irradiation fluence $\varphi > 10^{11}$ cm^{-2}, and PL intensity decreases faster than carrier lifetime.

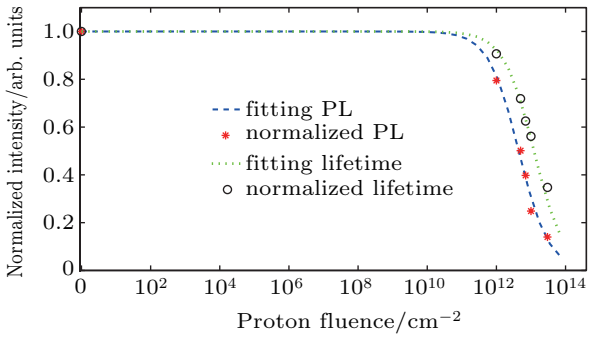


Fig. 4. (color online) Variations of normalized PL intensity and normalized lifetime of GaAs NWs with core diameter of 50 nm with irradiation fluence mainly ranging from 1.0×10^{12} p/cm^2 to 3.0×10^{13} p/cm^2. Both fitting data are also included.

Carrier lifetime is extremely important from a device-physics standpoint, because it governs the operation of semiconductor p–n junctions, one of the basic device structures, to a large extent.[32] In contrast to the bulk recombination lifetime, surface recombination is more sensitive to ionization damage, and only marginally to displacements.[32] Studies have also found that the AlGaAs shell acts as a passivation layer which could eliminate the surface states for GaAs NWs core.[29,38] One important point, however, is that the surface recombination is determined by the density of interface traps and the surface potential. Hence this study takes it into account that the surface recombination remains constant after

irradiation. On the other hand, Shockley–Read–Hall (SRH) recombination mechanism is typically used to discuss the recombination of electron-hole pairs at defect levels within the bandgap.[39] It has been usually described in the frame of the SRH theory,[37] in which the thermal (i.e., phonon-assisted) carrier transitions to and from the bands are considered. In principle, it can be extended to taking into account the contribution of different recombination centers, radiative lifetime, and the surface recombination lifetime. Hence, there is more than one deep-level defect present, and the total SRH lifetime of the NW at the low-injection level can be described by $\tau_{\rm SRH} = \sum_i 1/\tau_{\rm i}$. Therefore, the effective minority carrier lifetime can be written as

$$\frac{1}{\tau_{\rm mc}} = \frac{1}{\tau_{\rm R}} + \frac{4S_{\rm R}}{d} + \frac{1}{\tau_{\rm SRH}}, \tag{7}$$

where $S_{\rm R}$ and d are the surface recombination velocity and NW core diameter respectively, $\tau_{\rm i}$ is the SRH lifetime for type-i defect, and $\tau_{\rm R}$ is the radiative lifetime of minority carrier. In NWs, the minority carrier lifetime is dominated by the non-radiative lifetime, which is mainly determined by SRH. The reason is that the radiative lifetime is much longer than the non-radiative lifetime.[40,41] Then equation (7) can be given as

$$\frac{1}{\tau_{\rm mc}} \approx C_0 + \frac{1}{\tau_{\rm SRH}}, \tag{8}$$

where $C_0 = 1/\tau_{\rm R} + 4S_{\rm R}/d$ is treated as a constant principally for NWs with AlGaAs shell passivation. In addition, following the definition of SRH lifetime, one can write $\tau_{\rm SRH} = 1/\sigma N_{\rm t} \upsilon_{\rm th}$, where σ is the electron (hole) capture cross-section, $N_{\rm t}$ is the volume concentration of deep-level defects, and $\upsilon_{\rm th}$ is the thermal velocity of the electron (hole). Consequently, the effective minority carrier lifetime can be approximated in the following simple way[26]

$$\tau_{\rm mc} \propto \frac{1}{N_{\rm t}}, \tag{9}$$

which renders the analysis simpler when SRH recombination predominates. Accordingly, we could define a defect concentration creation rate $k_{\rm N}$, thus $N_{\rm t}(\varphi)$ and $N_{\rm t}(0)$ are the corresponding post- and pre-irradiated defect concentration and can be related by

$$N_{\rm t}(\varphi) = N_{\rm t}(0) + k_{\rm N}\varphi, \tag{10}$$

which indicates that the post-irradiated defect concentration varies linearly with irradiation proton fluence. The pre-irradiated defect concentration $N_{\rm t}(0)$ is a certain concentration of point defects of the starting NWs. Equation (10) in combination with Eq. (9), can be extended to defining a normalized defect concentration as

$$N_{\rm Normalized} = \frac{N_{\rm t}(\varphi)}{N_{\rm t}(0)} = 1 + \frac{k_{\rm N}}{N_{\rm t}(0)}\varphi \propto \frac{1}{\tau_{\rm Normalized}}. \tag{11}$$

From the above assumptions, the normalized defect concentration will be governed by both irradiation fluence and creation rate. It is also proportional to the reciprocal of normalized carrier lifetime. In a simple case, the linear relation coefficient between the normalized defect concentration and normalized carrier lifetime is 1. The fitting normalized defect concentration versus proton fluence is shown in Fig. 5. This result accords well with the previously reported result on the semi-insulating SI GaAs sample, which has shown that the defect concentration increases linearly with proton fluence.[42]

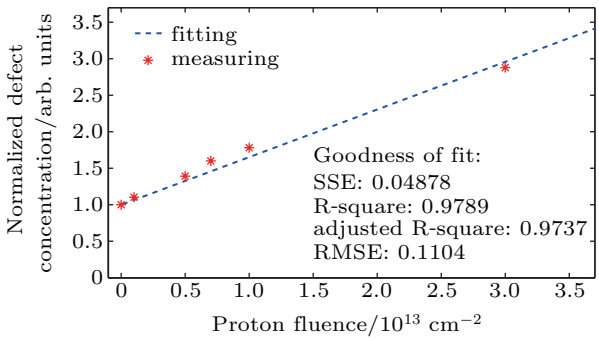


Fig. 5. (color online) Representative normalized defect concentration from Eq. (11) which is fitted through the data from measured normalized lifetime (blue dotted line). The fitting based on normalized defect concentration is directly proportional to the reciprocal of normalized lifetime on the assumption that the proportionality factor is 1 which renders the fitting simpler.

4. Conclusions

In summary, the radiation effect on GaAs/AlGaAs core-shell NWs with core diameter $\sim$ 50 nm is studied by proton irradiation in combination with the PL measurement technique. The model of relation between PL intensity degradation and minority carrier lifetime decline is obtained and explained under low photon injection and low proton irradiation fluence. Furthermore, the radiation effects on surface recombination and radiative recombination could be eliminated in the GaAs/AlGaAs core-shell NWs, and the irradiation-induced defect concentration can be extracted from the measurement of minority carrier lifetime. The results and their understanding achieved from this work will help further investigate irradiation-induced defects in nano-materials for space or atomic energy applications.

Acknowledgment

One of the authors is grateful to the Chinese Scholarship Council (CSC) for supporting him as a visiting student at the Australian National University (ANU) to conduct this research. The experimental work was mainly performed at the Department of Electronic Material Engineering, ANU with the help from all the students and staff in the Semiconductor Optoelectronics and Nanotechnology Group.

References

[1] Kato T, Susawa H, Hirotani M, Saka T, Ohashi Y, Shichi E and Shibata S 1991 *J. Cryst. Growth* **107** 832

[2] Stettner T, Zimmermann P, Loitsch B, Doblinger M, Regler A, Mayer B, Winnerl J, Matich S, Riedl H, Kaniber M, Abstreiter G, Koblmuller G and Finley J J 2016 *Appl. Phys. Lett.* **108** 011108

[3] Wei W, Liu Y G, Zhang X, Wang Z and Ren X M 2014 *Appl. Phys. Lett.* **104** 223103

[4] Badada B H, Shi T, Jackson H E, Smith L M, Zheng C L, Etheridge J, Gao Q, Tan H H and Jagadish C 2015 *Nano Lett.* **15** 7847

[5] Aberg I, Vescovi G, Asoli D, Naseem U, Gilboy J P, Sundvall C, Dahlgren A, Svensson K E, Anttu N, Bjork M T and Samuelson L 2016 *IEEE J. Photovolt.* **6** 185

[6] Seyedi M A, Yao M, O'Brien J, Wang S Y and Dapkus P D 2013 *Appl. Phys. Lett.* **103** 251109

[7] Seyedi M A, Yao M, O'Brien J, Wang S Y and Dapkus P D 2014 *Appl. Phys. Lett.* **105** 041105

[8] Yamaguchi M 2001 *Sol. Energy Mater. Sol. Cells* **68** 31

[9] Mitchell B, Trupke T, Weber J W and Nyhus J 2011 *J. Appl. Phys.* **109** 083111

[10] Marcinkevicius S, Leon R, Cechavicius B, Siegert J, Lobo C, Magness B and Taylor W 2002 *Physica B* **314** 203

[11] Ma L Y, Li Y D, Guo Q, Ai E K, Wang H J, Wang B and Zeng J Z 2015 *Acta Phys. Sin.* **64** 154217 (in Chinese)

[12] Zhou Y P, Li F J, Che C, Tan L Y, Ran Q W, Yu S Y and Ma J 2014 *Acta Phys. Sin.* **63** 148501 (in Chinese)

[13] Li F J, Tan L Y and Zhou Y P 2014 *Appl. Mech. Mater.* **556–562** 5163

[14] Andrievski R A 2014 *Uspekhi Fizicheskikh Nauk* **184** 1017

[15] Shen T 2008 *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **266** 921

[16] Tan H, Williams J, Jagadish C, Burke P and Gal M 1996 *Appl. Phys. Lett.* **68** 2401

[17] Tan H H and Jagadish C 1997 *Appl. Phys. Lett.* **71** 2680

[18] Fu L, Tan H H, Johnston M B, Gal M and Jagadish C 1999 *J. Appl. Phys.* **85** 6786

[19] Hirst L C, Yakes M K, Warner J H, Bennett M F, Schmieder K J, Walters R J and Jenkins P P 2016 *Appl. Phys. Lett.* **109**

[20] Stichtenoth D, Wegener K, Gutsche C, Regolin I, Tegude F J, Prost W, Seibt M and Ronning C 2008 *Appl. Phys. Lett.* **92** 163107

[21] Ronning C, Borschel C, Geburt S and Niepelt R 2010 *Mater. Sci. Eng. R* **70** 30

[22] Borschel C and Ronning C 2011 *Nucl. Instrum. Method B* **269** 2133

[23] Larin F 1968 *Radiation Effects in Semiconductor Devices* (New York, London, Sydney: John Wiley & Sons) p. 2

[24] Johnson N M, Ponce F A, Street R A and Nemanich R J 1987 *Phys. Rev. B* **35** 4166

[25] Brauer G, Anwand W, Skorupa W, Kuriplach J, Melikhova O, Moisson C, von Wenckstern H, Schmidt H, Lorenz M and Grundmann M 2006 *Phys. Rev. B* **74** 045208

[26] Li J, Li Z Y, Tan L Y, Zhou Y P, Ma J, Mykhaylo L, Fu L, Tan H H and Jagadish C 2017 *Nanotechnology* **28** 125702

[27] Jiang N, Gao Q, Parkinson P, Wong-Leung J, Mokkapati S, Breuer S, Tan H, Zheng C, Etheridge J and Jagadish C 2013 *Nano Lett.* **13** 5135

[28] Jiang N, Parkinson P, Gao Q, Breuer S, Tan H, Wong-Leung J and Jagadish C 2012 *Appl. Phys. Lett.* **101** 023111

[29] Joyce H J, Parkinson P, Jiang N, Docherty C J, Gao Q, Tan H H, Jagadish C, Herz L M and Johnston M B 2014 *Nano Lett.* **14** 5989

[30] Joyce H J, Gao Q, Tan H H, Jagadish C, Kim Y, Zhang X, Guo Y and Zou J 2007 *Nano Lett.* **7** 921

[31] Ju S, Lee K, Janes D B, Dwivedi R C, Baffour-Awuah H, Wilkins R, Yoon M H, Facchetti A and Mark T J 2006 *Appl. Phys. Lett.* **89** 073510

[32] Claeys C and Simoen E 2013 *Radiation effects in advanced semiconductor materials and devices* (New York: Springer Science & Business Media) p. 33

[33] Simoen E, Vanhellemont J and Claeys C 1996 *Appl. Phys. Lett.* **69** 2858

[34] Markvart T 1990 *J. Mater. Sci.: Mater. Electron.* **1** 1

[35] Vanhellemont J, Simoen E, Claeys C, Kaniava A, Gaubas E, Bosman G, Johlander B, Adams L and Clauws P 1994 *IEEE Trans. Nucl. Sci.* **41** 1924

[36] Watts S J, Matheson J, HopkinsBond I H, HolmesSiedle A, Mohammadzadeh A and Pace R 1996 *IEEE Trans. Nucl. Sci.* **43** 2587

[37] Schroder D K 1997 *IEEE Trans. Electron. Dev.* **44** 160

[38] Lauhon L J, Gudiksen M S, Wang D and Lieber C M 2002 *Nature* **420** 57

[39] Sah C T, Noyce R and Shockley W 1957 *Proc. IRE* **45** 1228

[40] Liu H C, Wilson P H, Buchanan M and Khanna S M 1996 *Infrared Detectors and Focal Plane Arrays Iv* **2746** 134

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

[42] Ferrini R, Galli M, Guizzetti G, Patrini M, Nava F, Canali C and Vanni P 1997 *Appl. Phys. Lett.* **71** 3084