Exp. Theo. NANOTECHNOLOGY 5 (2021) 23 – 32 https://doi.org/10.56053/5.2.23

Optical studies of InAs/GaAs quantum dot stacks for photovoltaic applications

J. Yang[1,*], *M. V. Reddy*[2]

[1]Department of Mechanical & Materials Engineering, Western University, 3089 Ontario, Canada
[2]Institute of Research Hydro-Quebec, Montreal, Canada
[*]) E-mail: yangj@uwo.ca

Received 13/3/2020, *Accepted* 25/7/2020, *Published* 15/5/2021

We have investigated the effect of post growth rapid thermal annealing on self-assembled InAs/GaAs multilayer QDs (MQD) overgrown with a combination barrier of InAlGaAs and GaAs for their possible use in photovoltaic device application. The samples were characterized by transmission electron microscopy and photoluminescence measurements. We noticed a thermally induced material interdiffusion between the QDs and the wetting layer in the MQD sample up to a certain annealing temperature. The QD heterostructure exhibited a thermal stability in the emission peak wavelength on annealing up to 700 °C. A phenomenological model has been proposed for this stability of the emission peak. The model considers the effect of the strain field, propagating from the underlying QD layer to the upper layers of the multilayer QD and the effect of indium atom gradient in the combination barrier layer due to the presence of a quaternary InAlGaAs layer.

Keywords: InAs/GaAs; QDs; Optical; PVs.

1. INTRODUCTION

With the introduction of nanostructure based intermediate band solar cell (IBSC), the search for photovoltaic de- vices that can operate at high concentration resulting in high power conversion efficiency attained a new dimension. Self-assembled quantum dots (QDs) grown under Stranski–Krastanov (S-K) growth mode have evoked a great zeal over last few years in photovoltaic device application in the form of quantum dot intermediate band solar cell (QD-IBSC), which constitutes the third generation of solar cells [1–4]. In an IBSC, an intermediate band (IB), which is half-filled with electrons exists between the valence band (VB) and the conduction band (CB). Thus, in addition to absorbing photons with energy greater than the bandgap, photons with lower energies can also be harvested by electronic transitions between the VB and the IB, and the IB and CB. In a QD-IBSC, the IB is formed with the introduction of valid quantum states of the QD deep into the previously forbidden band gap of a host semiconductor and can be used for ab- sorption of incident photons in the solar spectrum at energies below the band gap of the GaAs host matrix [5]. The ground state emission peak of InAs/GaAs QD lies typically in be- tween 900 nm to 1200 nm [6,7]. Hence, the use of InAs QD in IBSC will enable a larger portion of the long wavelength region of solar radiation spectrum to be harvested for the photocurrent generation. This will increase the photovoltaic conversion efficiency of the solar cells to much higher values; at the same time will maintain a high open-circuit volt- age due to the large bandgap GaAs electrodes. A typical InAs/GaAs QD-IBSC device will consist of a standard p-i-n device structure with layers of InAs/GaAs QDs separated by different types of strain reducing barrier layers [8, 9].

GaAs window layer is to be grown over the top of GaAs solar cells. The AlGaAs layers are usually grown at temperatures higher than the growth temperature of the InAs/GaAs QDs [12, 13]. Thus, it becomes imperative to study the morphology and optical properties of InAs/GaAs MQDs subjected to high temperature annealing treatment. Furthermore, thermal annealing of vertically stacked QD layers can also be used to relax the strain energy accumulated in the device structures by atomic interdiffusion of materials, and thus to im- prove the device performance. Moreover, annealing reduces nonuniformities in QD sizes leading to the formation of a more uniform intermediate band throughout the active region of the device. This may enhance the absorption cross- section of the solar cells leading to enhancement in efficiency. It is expected that activation energy of the QDs, i.e., the energy difference between confined level of the QD and the band edge of barrier layer will change as a result of annealing process. However, excessive high temperature (i.e., 700 ◦C) annealing degrades the quantum confinement effects in the QD structure due to defect generation caused by thermal damage. In this study, we have investigated the annealing induced change in the microstructural and optical property of a 10-layer MQD heterostructure where the QD stacks are separated by a combination barrier of In0.21Al0.21Ga0.58As and GaAs. The main pur- pose of using this particular composition for the quaternary alloy InAlGaAs is that its lattice parameters and the band gap energy almost matches with that of the GaAs which in turn helps in minimizing the disadvantages of dot in a well (DWELL) structure in the samples. A careful investigation of the annealing induced changes in the above mentioned MQD structure will ensure the incorporation of such structures as an active element in IB solar cells.

2. EXPERIMENTAL

The self-assembled InAs/GaAs MQD sample used in the study was grown by solid source molecular beam epitaxy (MBE) on a semi insulating (001) GaAs substrate. The 2.7 ML InAs QDs in the 10-layer stacked heterostructure were grown at a 0.2 ML/sec growth rate at 520 ◦C. The QDs were overgrown with a combination capping of 30 Å quaternary In0.21Al0.21Ga0.58As and a thick GaAs spacer (180 Å) grown at 520 ◦C. The capping layers were subsequently annealed at 590 ◦C. Details of the sample growth can be found in [10]. Small pieces were cut from the central region of the MBE grown wafer and were subjected to ex situ rapid thermal annealing (RTA) under GaAs proximity capping in argon ambient. This keeps the surface of the annealed samples unaffected due to annealing procedure by minimizing the out diffusion of As from the sample surface at high temperatures [14]. The samples were annealed for duration of 30 s at different annealing temperatures in Anneals AS-ONE 150 RTP system. The samples for cross-sectional transmission electron microscopy (XTEM) observations were prepared by conventional mechanical polishing and ion milling techniques. It is then observed with a TEM microscope under an acceleration voltage of 200 kV. The Photoluminescence (PL) experiment has been carried out at 8 K with the sample mounted in a continuous flow He-cryostat using 405 nm ex- citation wavelength. A liquid nitrogen cooled InGaAs array detector is used for detection of the PL signal dispersed by a 0.75 nm monochromator. Power dependent PL was done at 8 K with different laser powers ranging from 0.5 mW to 25 mW.

3. RESULTS AND DISCUSSION

The microstructure and morphology of the as-grown and annealed samples were studied using TEM. The occurrence of spatial correlation in the vertical direction between the ad- jacent QD stacks can be observed from microscopy images. The randomly distributed inhomogeneous strain field [15, 16] produced by the underlying QDs can be attributed for the vertical coupling between layers as it provides the driving force for the nucleation of the upper QDs. It is to be mentioned here that on increasing the number of QD stacks the overall accumulated homogeneous strain in the heterostructure increases [10], which limit the stacking number in a multilayer QD system. The micrograph of as-grown sample in Fig. 1 indicates clear formation of QD stacks. Defect free stacked QD structure is also observed for the sample annealed at 650 ◦C in Fig. 1. Figure 1 illustrates that the QDs are present even after annealing at 750 ◦C temperature while due to intermixing their sizes are reduced. Figure 1 shows that upon annealing at 850 ◦C the QDs starts dissolving in the surrounding wetting layer.

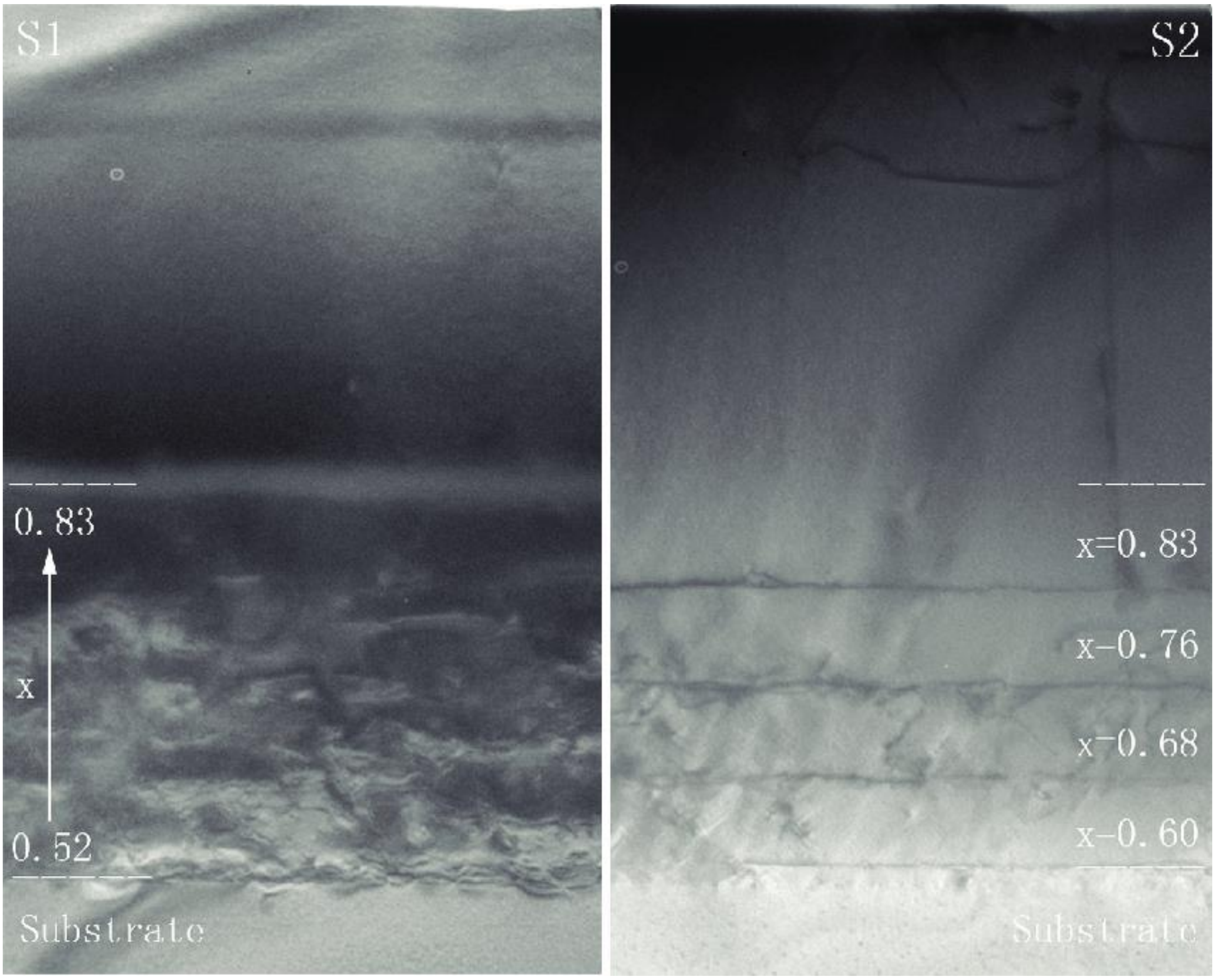

Figure 1 XTEM images of themultilayer QDs as-grownand annealed at different temperatures.

To study the emission properties of as-grown and the annealed samples, we have done photoluminescence spectroscopy. Figures 2 shows the PL spectra of the as-grown, and 650 ◦C, 700 ◦C, 750 ◦C annealed sample with different laser powers ranging from 0.5 mW to 25 mW at 8 K. It is to be noted here that the maxi- mum laser power with which the samples were being excited is kept low and there is hardly any noticeable shift of the PL peaks with increasing laser power. This indicates that while recording the PL data there is no power dependent uncertainty in the PL spectrum due to warming of the sample region under the optical excitation. In Fig. 2, we can see that with an increase in the excitation power the overall intensity of the peaks at 0.97 eV, 1.01 eV, and 1.107 eV is enhanced, whereas for the PL peaks at 1.05 eV and 1.2 eV there is a change in the relative intensity with excitation power which can only be related to emission from the excited states observed. The emergence of these multiple peaks in the PL spectrum may be due to the multimodal distribution of the QDs in the as-grown sample. From our previous work [10] on stacked InAs/GaAs MQD, it can be presumed that one of the peaks in the PL spectrum of Fig. 2 might have resulted due to emission of the QDs present in the incomplete stacks of the MQD sample. By applying similar reasoning as above, we can easily make out from the power dependent plots of Fig. 2 that the peaks at 0.97 eV, 0.97 eV, and 1.12 eV are due to the emission from the ground state and the 1.05 eV, 1.05 eV, and 1.175 eV peaks are due to the emission from the excited states in the respective PL plots. Further, the FWHM of the 0.97 eV ground state PL peak at 1 mW excitation laser power in Fig. 2 for the 650 ◦C and 700 ◦C annealed MQD sample is found to be of the order of 34 meV. Thus, by tracing the PL evolution of QDs with variation in excitation power, we can say that annealing the MQD sample leads to uniform QD size distribution. We consider that on annealing there is a thermally induced material interdiffusion between the QDs and the wetting layer up to a certain annealing temperature, leading to uniformity/homogenization in the dot size distribution. The shift in the PL ground state peak to shorter wavelength at 1.12 eV with reduced intensity for the 750 ◦C annealed sample can be related with increased In/Ga inter- mixing between the QDs and the barrier, and dissolution of dots in the wetting layer which are the usual occurrences in InAs QD structure [14].

The 8 K PL spectrum of the as-grown sample and the sample annealed at different temperatures at 1 mW excitation power are depicted. Since the laser power is kept at a low value (1 mW), only the ground state PL peaks are revealed in the figure. A remarkable observation from the PL spectrum of the sample annealed at different temperatures is that no prominent blue-shift is observed in the emission peak at higher energy side of the PL spectrum up to 700 ◦C. This is quite unusual for InAs/GaAs quantum dot system where pronounced blue-shift is observed due to annealing as a result of In/Ga interdiffusion between the dot and the barrier [14, 17, 18].

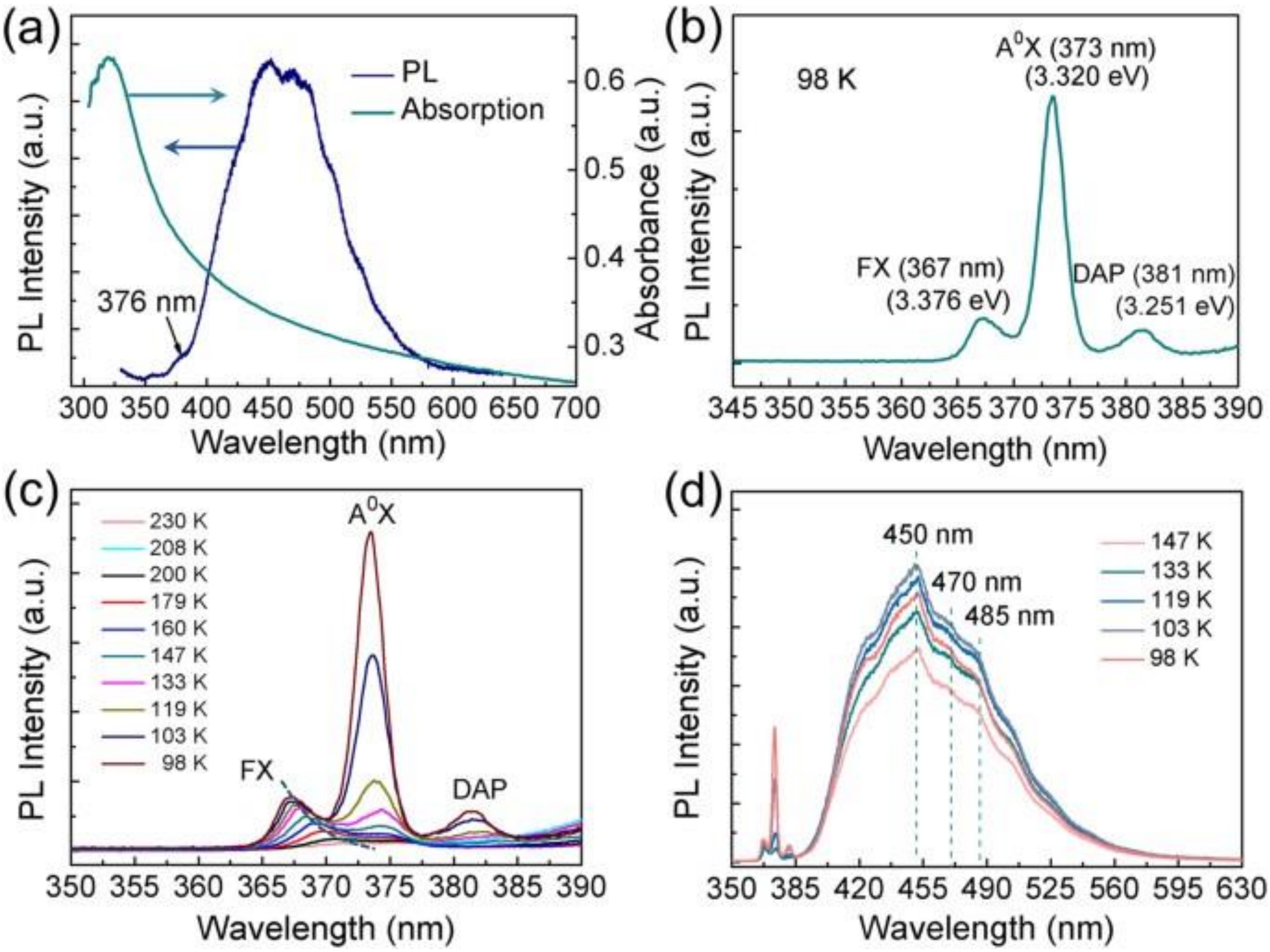

Figure 2 Power dependent PL spectra of unannealed and annealed at different temperatures.

Even both coupled [19–21] and uncoupled [22] QD stacks are reported to have significant shift in the emission peaks upon annealing at higher temperatures (>600 ◦C). This stability in the PL emission peak of the MQD sample due to annealing up to 700 ◦C makes such heterostructure useful in fabrication of IBSCs where the window layer is grown at higher temperature (>590 ◦C) [12,13]. In Fig. 3, the activation energies of annealed samples are calculated considering the variation of overall PL signal from the samples with temperature and are plotted against the corresponding annealing temperature. The characteristic equation used for the calculation of the activation energy is similar to that mentioned in [23]. The plot shows a gradual reduction in the activation energy on annealing the samples beyond 650 ◦C indicating the degradation of the crystalline quality of the sample on annealing at temperatures above 650 ◦C. Based on the above mentioned observations of TEM and PL experiments, we propose that the stability of the peak emission wavelength in the MQD samples subjected to post growth annealing up to 700 ◦C is due to two complimentary effects which prevents the In/Ga intermixing between the QDs and the combination barrier.

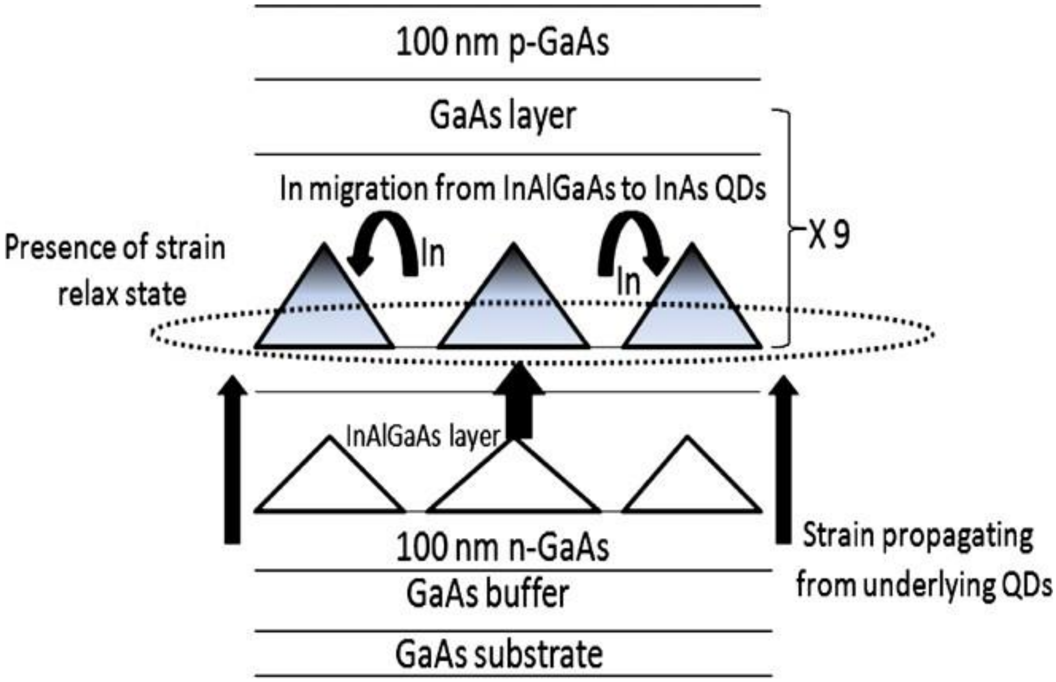

Figure 3 Diagram describing the thermal stability during annealing and annealed at different temperatures.

The InGaAlAs layer which constitutes the combination barrier, results in In concentration gradient across the periphery of the InAs islands due to the directional migration of the In adatoms from quaternary alloy toward the QDs during growth of the samples; the detailed mechanism is described elsewhere [10,11]. This gradient prevents the inter- mixing of the QDs with the barrier material in the structure during annealing, preserving the shape of the QDs at high annealing temperature (as can be seen from the TEM images of Fig. 1). Simultaneously, the inhomogeneous strain field [15,16] propagating from the underlying layers to the upper QD layers plays an important role in stability of the emission peak. The strain relaxed state of the QDs in the heterostructures which is maintained by the strain field propagating along the QD stacks in the growth direction might be one of the reasons for thermal stability. This strain re- laxation due to vertical stacking of QDs prevents the In/Ga intermixing at the base of the QDs where the misfit strain is reported to be maximum. Thus, the emission peak blueshift which is a usual phenomenon during annealing of QD heterostructures is checked in the grown MQD sample due to the above-mentioned complementary effects. Further, there is homogenization of QD size due to annealing, as a result of In atom redistribution between the QDs and the wetting layer. But as the samples are annealed at higher temperatures, the thermally driven In/Ga intermixing surpasses the above mentioned effects resulting in significant blueshift.

4. CONCLUSIONS

In conclusion, we have studied the effect of annealing on the morphology and emission properties of stacked InAs/GaAs QDs over grown with a combination barrier of InAlGaAs and GaAs for their possible use in the fabrication of inter- mediate band solar cell. The TEM micro-graphs showed that shape of the QDs were preserved even annealing beyond 750 °C temperature. We noticed a thermally induced material interdiffusion between the QDs and the wetting layer in the MQD sample up to a certain annealing temperature. A thermal stability in emission peak is observed in the MQD sample on annealing up to 700 °C which makes the sample useful for photovoltaic device fabrication as the window layer in such devices are grown at temperatures higher than the growth temperature of the InAs QDs. We propose that the stability in the peak emission wavelength is due to the overgrown quaternary InAlGaAs alloy which prevents the usual intermixing in such structures by forming an Indium gradient across the QD periphery. The strain relaxed state at the base of the InAs QDs which is due to the overlapping strain from the vertical stacks also suppresses the In/Ga intermixing thereby stabilizing the emission peak wavelength in such structures.

References

[1] A. Babinski, J. Jasin´ski, R. Bozek, A. Szepielow, J.M. Baranowski, Appl. Phys. Lett. 79 (2001) 2576
[2] X.F. Yang, K. Fu, W. Lu, W.L. Xu, Y. Fu, J. Phys. D, Appl. Phys. 42 (2009) 125414
[3] S. Chakrabarti, N. Halder, S. Sengupta, S. Ghosh, T.D. Mishima, C.R. Stanley, Nanotechnology 19 (2008) 505704
[4] S.J. Xu, X.C. Wang, S.J. Chua, C.H. Wang, W.J. Fan, J. Jiang, X.G. Xie, Appl. Phys. Lett. 72 (1998) 3335
[5] X.C. Wang, S.J. Xu, S.J. Chua, Z.H. Zhang, W.J. Fan, C.H. Wang, J. Jiang, X.G. Xie, J. Appl. Phys. 86 (1999) 2687
[6] J. Tatebayashi, N. Hatori, M. Ishida, H. Ebe, M. Sugawara, Y. Arakawa, H. Sudo, A. Kuramata, Appl. Phys. Lett. 86 (2005) 053107
[7] H.S. Lee, J.Y. Lee, T.W. Kima, M.D. Kim, J. Appl. Phys. 94 (2003) 6354
[8] C.Y. Leea, J.D. Songa, Y.T. Leea, T.W. Kimb, Solid State Com- mun. 126 (2003) 421
[9] E. Nabavi, T.J. Badcock, T. Nuytten, H.Y. Liu, M. Hopkinson, V.V. Moshchalkov, D.J. Mowbray, J. Appl. Phys. 105 (2009) 053512
[10] S. Sengupta, N. Halder, S. Chakrabarti, Mater. Res. Bull. 45 (2010) 1593
[11] N. López, A. Martí, A. Luque, C. Stanley, C. Farmer, P. Diaz, J. Sol. Energy Eng. 129 (2007) 319
[12] S. Sengupta, N. Halder, S. Chakrabarti, Superlattices Microstruct.46 (2009) 611
[13] N. Halder, S. Chakrabarti, C.R. Stanley, J. Nanosci. Nanotechnol. 8 (2008) 6232
[14] R.B. Laghumavarapu, M.E. Emawy, N. Nuntawong, A. Moscho, L.F. Lester, D.L. Huffaker, Appl. Phys. Lett. 91 (2007) 243115
[15] V. Popescu, G. Bester, M.C. Hanna, A.G. Norman, A. Zunger, Phys. Rev.B 78 (2008) 205321
[16] S. Adhikary, N. Halder, S. Chakrabarti, S. Majumdar, S.K. Ray, M. Herrera, M. Bonds, N.D. Browning, J. Cryst. Growth 312 (2010) 724
[17] N. Halder, J. Suseendran, S. Chakrabarti, M. Herrera, M. Bonds, N.D. Browning, J. Nanosci. Nanotechnol. 10 (2010) 5202
[18] F.G. Ragay, M.R. Leys, P.A.M. Nouwens, W.C.V. Vleuten, J.H. Wolter, IEEE Electron Device Lett. 13 (1992) 618
[19] S. Suraprapapich, S. Thainoi, S. Kanjanachuchai, S. Panyakeow, Sol. Energy Mater. Sol. Cells 90 (2006) 2968
[20] Abraham George, Exp. Theo. NANOTECHNOLOGY 5 (2021) 37

[21] Zain A. Muhammad, Tariq J. Alwan, Exp. Theo. NANOTECHOLOGY 5 (2021) 47
[22] Aseel I. Mahmood, Shehab A. Kadhim, Nadia F. Mohammed, Intisar A. Naseef, Exp. Theo. NANOTECHNOLOGY 5 (2021) 57
[23] Abdulrahman Khaleel Suliman, Mustafa Saeed Omar, Exp. Theo. NANOTECHNOLOGY 5 (2021) 65