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ABSTRACT

The effect of a post-growth thermal treatment in two different heterostructures with InAlAsSb as the top layer grown by molecular beam epitaxy lattice-matched to InP, have been studied by diffraction contrast transmission electron microscopy (TEM).[1] This novel top cell layer material with application in ultra-high efficiency solar cells were grown on (001) InP substrate with or without an InGaAs buffer layer. Initial photoluminescence (PL)[2] measurements revealed deviations from their predicted bandgap, suggesting non-random atomic distribution of the quaternary layer. Then, a thermal annealing was performed at different temperatures and times. The effect on the structure of the InAlAsSb active layer caused by the new arrangement of layers and the post-growth annealing treatments has been reported. Our results show that the small compositional fluctuations of the as-grown heterostructures disappear after being annealed, and the bandgap energy correspondingly increases towards the predicted value.

1. Introduction

Major advances in the field of semiconductors, together with a great progress in the techniques of materials growth have made possible the development of the so-called *bandgap engineering*. These design strategies provide a variety of bandgap tuned systems optimized, among others, to solar energy applications. III–V multijunction solar cells have held record efficiency for the past few decades, with a current highest value of 46% for a mechanically stacked 4 junction (4J)[3] device under concentrated terrestrial sunlight [1]. When grown monolithically, the record efficiency is 45.7%, also for a 4 J inverted metamorphic (IMM)[4] III–V solar cell grown on GaAs substrates [1]. In this method, some of the layers are grown under mismatch conditions to better match the ideal bandgap for solar energy conversion. However, due to the difference in lattice constant, crystalline defects will form in layers mismatched to their binary substrates. An alternative approach is to move towards the InP-based material system where the use of quaternary alloys, allow for different energy bandgaps while maintaining lattice matching conditions and hence circumventing this problem. Within this context, the quaternary alloy InAlAsSb matched to InP is gaining interest for the top layer of 3 junction (3J) solar cell concentrators, because of its direct bandgap range, expecting to get a value of 1.8 eV [2].

The PL features of the 1 μm InAlAsSb layer, epitaxially grown on a 200 nm InGaAs buffer layer, revealed deviations from its predicted bandgap [3]. Furthermore, micrographs taken in [220] bright field conditions depicted the existence of strain fluctuations in the buffer layer, related to compositional modulation for all studied growth conditions. Aberration corrected scanning transmission electron microscopy (STEM)[5] studies showed the possibility of short range compositional fluctuation in quaternary layers [4]. Non-random growth in InAlAsSb heterostructures lattice-matched to InAs has been reported previously [5].

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[1] TEM: transmission electron microscopy

[2] PL: photoluminescence

[3] 4J: 4 junction

[4] IMM: inverted metamorphic

[5] STEM: scanning transmission electron microscopy

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It is well-known that composition modulation in III–V semiconductor broadens photoluminescence curves reducing their efficiency [6]. Furthermore, the thickness and composition of the buffer also affects to the compositional modulation [7]. So, the knowledge of growth conditions that cause compositional fluctuations is essential to optimize the performance of these optoelectronic devices [6,8–10]. In order to surpass these limitations, new InAlAsSb heterostructures lattice-matched to InP were grown without an initial InGaAs buffer layer and combined with post thermal treatments to optimize their optoelectronic properties.

Bright field imaging under two beam conditions in conventional TEM has been widely used to obtained information about crystalline quality and compositional modulations in semiconductor materials. [14,21–24] Although many evidences in literature have shown the ability to quantify composition in ternary semiconductors grown on binary substrates, using high angle annular dark field (HAADF) [25–28] and electron energy loss spectroscopy (EELS) [29–33] techniques, in quaternary alloys due to that both cat-ion and an-ion can segregate simultaneously, the influence of neighbour column in the intensity value and the intrinsic 2D projection of these techniques make not reliable the quantification of small compositional fluctuations within these hetero-structures so far [4].

We report here the characterization of InGaAs/InAlAsSb/InGaAs/InP and InGaAs/InAlAsSb/InP heterostructures grown by molecular beam epitaxy (MBE)[6] at different annealing conditions by conventional TEM techniques. Samples before and after annealing treatments are compared, correlating structure with optoelectronic properties.

2. Material and methods

Different lattice-matched In$_x$Al$_{1-x}$As$_y$Sb$_{1-y}$ samples were grown on InP substrates with (PB samples) and without InGaAs buffer layer (P samples). In order to achieve lattice matching, the In and As compositions in the quaternary layer is within the range of $0.15 < x < 0.20$ and $0.69 < y < 0.73$. The samples were grown in an As-Sb molecular beam epitaxy (MBE) system at a substrate temperature of 450 °C. After the growth the samples were transferred to a metal organic chemical vapour deposition (MOCVD)[7] system where they were annealed under As overpressure. Table 1 shows the layering of the studied samples and the conditions of the post-annealed treatments.

Electron transparent TEM samples were prepared in cross section by focused ion beam (FIB),[8] using a FEI Quanta 200 3D model. The upper layer of the sample was previously covered with a thin Pt layer to avoid damage during the Ga$^+$ bombardment. Before TEM analysis all samples were plasma cleaned [11]. The TEM study was performed using a JEOL JEM 1400 operating at 100 kV.

PL spectroscopy was performed using a focused 532 nm photoexcitation laser. The PL signal was spectrally analysed with Princeton Instruments Acton 2500 spectrometer and cooler Si array. The stability of the samples surface has been checked before and after annealing treatments by optical inspection.

In order to know structural defects in the lattice or disorder caused by variations in the chemical composition of the layers, all the samples were characterized using diffraction contrast technique in two-beam conditions 220 bright field (BF),[9] being this reflection sensitive to displacement in (220) atomic planes. The compositional modulation is observed in these images as dark and light stripes parallel to the [001] growth direction.

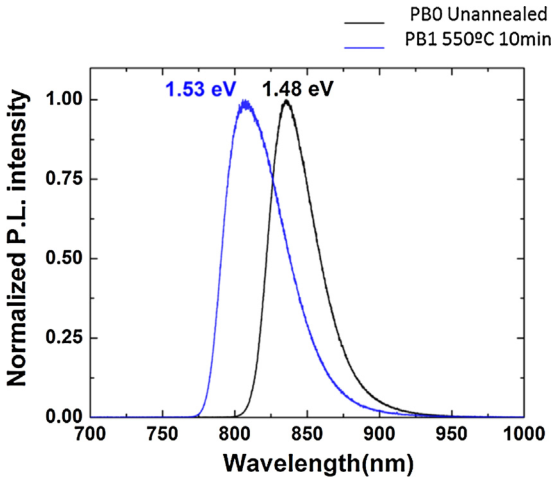

Fig. 1. PL spectra of PB sample at 5 K before and after annealing study, a blue-shift in the peak emission is observed.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

Fig. 1 shows the PL measured at 5 K of the InGaAs/InAlAsSb/InGaAs/InP undoped heterostructure related to the unannealed control sample (PB0, black line in the graphic) and the thermal treated one (PB1, blue). Fig. 1 points out a blue-shift effect in PL signal as annealing temperature and exposure time increases with respect to the unannealed sample. This is consistent with studies performed via rapid thermal annealing on similar material [12]. Additionally, post-growth annealing at 500 °C for 60mins under As overpressure was performed on the n-doped sample P1, with a resulting blue shift of 1.46 eV (P0) to 1.59 eV (P1). Additional annealing experiments are underway in this material and the results will be presented elsewhere. Optical inspection of the sample surface depicted stable surface morphology after annealing in every sample, even at such a long annealing time of 60 min (P1).

Fig. 2 shows 220BF diffraction contrast images of the samples PB0 A) and PB1 B). Faint strain contrast in both InAlAsSb and InGaAs layers are observed in PB0 sample. This is a well-known contrast associated to small compositional fluctuations [9,10,13,14]. This contrast was not found in the PB1 sample. The study revealed that a post annealing treatment under As overpressure at 550° for 10 min of the InGaAs/InAlAsSb/InGaAs/InP heterostructure reduces the composition fluctuations in ternary and quaternary layers and consequently shifts the bandgap energy from 1.48 eV to 1.53 eV.

Fig. 3A) shows 220BF diffraction contrast images of the InP/InGaAs/InAlAsSb heterostructure of the control sample P0, revealing the presence of a stacking fault (SF) across the quaternary and ternary layers. In this micrograph quasi-periodic strain contrast near the interfaces are also observed, this contrast is a typical feature of compositional modulation. Fig. 3B) and C) shows 220BF diffraction contrast images of the P1 sample (annealed at 500 °C for 60 min under As overpressure) corresponding to the interfaces InGaAs/InAlAsSb and InP/InGaAs respectively, showing the absence of strain contrast generated by composition variations near the interfaces.

In light of the obtained results it seems that the post-growth annealing treatment at 500 °C for 60 min of the InGaAs/InAlAsSb/InP heterostructure stimulates the atomic diffusion of the alloy constituents towards reducing the compositional

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[6] MBE: molecular beam epitaxy
[7] MOCVD: metal organic chemical vapour deposition
[8] FIB: focused ion beam
[9] BF: bright field

Table 1
Sample structure, composition, thickness of each layer and annealing conditions.

Sample	Structure and Composition	Thickness (nm)	Dopant	Annealing
PB0	$In_{0.53}Ga_{0.47}As$	25	Undoped	Unannealed
	$In_xAl_{1-x}As_ySb_{1-y}$	1000	Undoped	
	$In_{0.53}Ga_{0.47}As$	25	Undoped	
	InP			
PB1	$In_{0.53}Ga_{0.47}As$	25	Undoped	550 °C
	$In_xAl_{1-x}As_ySb_{1-y}$	1000	Undoped	10 min
	$In_{0.53}Ga_{0.47}As$	25	Undoped	
	InP			
P0	$In_{0.53}Ga_{0.47}As$	20	Si: 3×10^{18}–5×10^{18} (n)	Unannealed
	$In_xAl_{1-x}As_ySb_{1-y}$	1000	Si: 1×10^{17}–5×10^{17} (n)	
	InP			
P1	$In_{0.53}Ga_{0.47}As$	20	Si: 3×10^{18}–5×10^{18} (n)	500 °C
	$In_xAl_{1-x}As_ySb_{1-y}$	1000	Si: 1×10^{17}–5×10^{17} (n)	60 min
	InP			

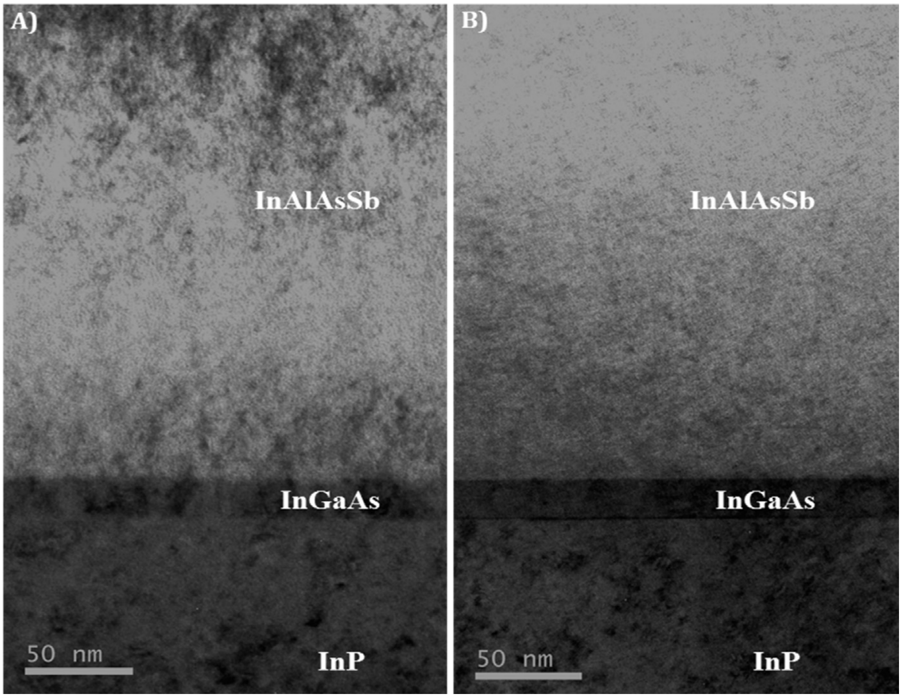

Fig. 2. A) 220BF TEM micrograph of the heterostructure InP/InGaAs/InAlAsSb of sample PB0 (unannealed) reveals weak columnar-like contrast in both the ternary buffer layer and the quaternary layer. B) 220BF micrograph of the interface InP/InGaAs/InAlAsSb of sample PB1 (post-growth annealed at 550 °C for 10 min), showing that strain contrast in ternary and quaternary layers disappear after the annealing process.

modulation. The typical dark light contrast of compositional modulated layers is almost insignificant in the thermally treated sample, leading to the increase the energy bandgap from 1.46 eV to 1.59 eV.

The use of a post-growth annealing step to energize atomic diffusion within the crystal lattice and increase the optical efficiency of the optoelectronic devices has been successful in reducing segregation in dilute nitride materials which exhibit similar photoluminescence behaviour [15,16]. Several references in the literature have reported a PL blue-shift in epitaxially grown heterostructures after thermal annealing, due to the redistribution of the nearest-neighbour configuration, [17] the inter-diffusion of the atoms in the alloy [18] or the annihilation of point defects. [19] Furthermore, the insertion of dopants in semiconductors alloys to eliminate phase-separation or ordering is another technique widely used, for example during InAlP/InGaAs/GaAs growth [20].

Regarding the buffer layer, we can confirm in the studied samples that the presence of compositional modulation in the quaternary InAlAsSb is independent of the presence of an InGaAs decomposed underneath [4]. This buffer layer may also have some benefits on securing a defect free quaternary growth, but this has to be checked with a wider statistical study. It is worth commenting that this buffer layer is beneficial from the functional point of view to block PL emission from substrate and reduce series resistance value on the final device.

Hence, post-growth annealing allows to achieve good quality InAlAsSb layers at higher Al contents and lower temperatures than the limits observed by Semenov et al. In comparison to the previous results in [3] where the quaternary layer showed an anomalously low PL emission peak energy, this strategy consisting to a different layer structure and composition with higher aluminium content increases the bandgap energy.

4. Conclusion

In this work heterostructures for MJ solar cells using the novel quaternary InAlAsSb lattice matched to InP as the active layer and

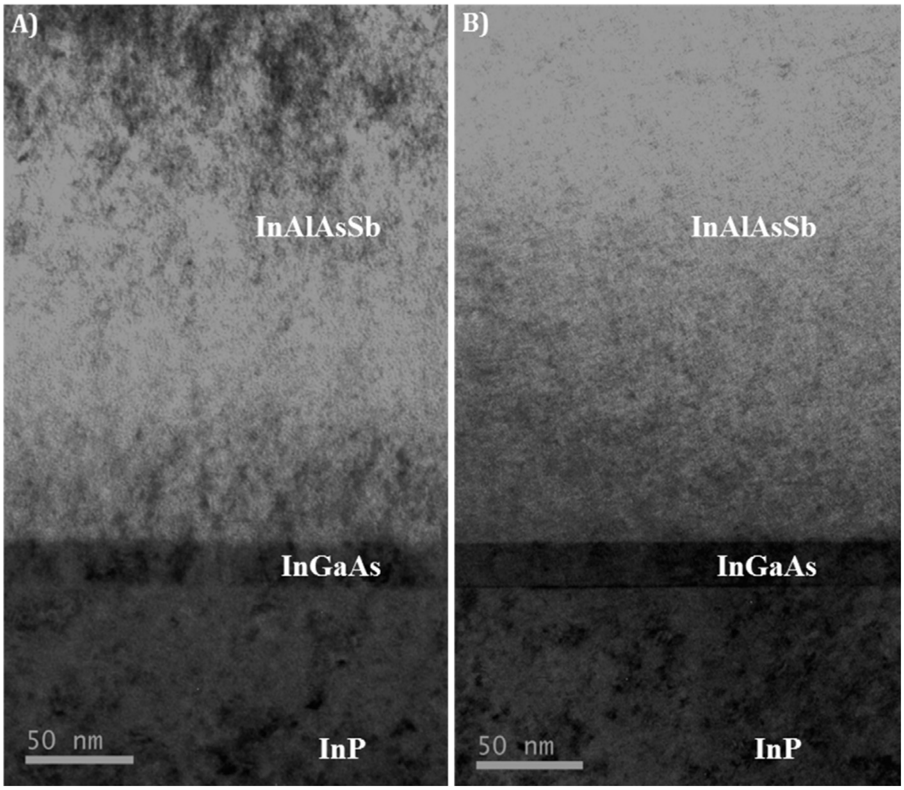

Fig. 3. A) 220BF TEM micrograph of the heterostructure InGaAs/InAlAsSb/InP of the non-annealed sample (P0), showing a planar defect (SF) across InAlAsSb and InGaAs layers and the presence of strain contrast in both layers. B) and C) 220BF TEM micrographs of P1 sample, taken from InGaAs/InAlAsSb and InP/InGaAs interfaces respectively, revealing the lack of strain contrast and crystalline defects in ternary and quaternary layers.

subjected to different thermal annealing conditions over As pressure are analysed. Two series of samples, with InGaAs buffer layer (PB samples) and without buffer layer (P samples), were characterized by PL measurements and TEM diffraction contrast imaging. Small strain fluctuations appear in both heterostructures. However, after being submitted to a post-growth annealing process under As overpressure over 500 °C for several minutes, they experience a blue-shift together with a mitigation of the compositional modulation.

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References

[1] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Solar cell efficiency tables (version 47) (vol 24 pg 3–11, 2016), Prog. Photovoltaics 24 (2016) 3–11.
[2] M. Gonzalez, M.P. Lumb, M.K. Yakes, C.G. Bailey, J.G. Tischler, R. Hoheisel, J. Abell, I. Vurgaftman, J. Meyer, S. Maximenko, P.P. Jenkins, S.I. Molina, F.J. Delgado-Gonzalez, D. Bahena, A. Ponce, J.G.J. Adams, M. Fuhrer, N. Ekins-Daukes, R.J. Walters, Towards high efficiency multi-junction solar cells grown on InP substrates, in: Ieee 39th Photovoltaic Specialists Conference (Pvsc), 2013, 2013, pp. 145–148.
[3] S. Tomasulo, M. Gonzalez, J.G. Tischler, J. Abell, M.P. Lumb, M.K. Yakes, L.C. Hirst, F.J. Delgado-Gonzalez, M. Herrera, S.I. Molina, I. Vurgaftman, J.R. Meyer1, R.J. Walters, Molecular beam epitaxy of InAlAsSb for the top cell in high-efficiency InP-based lattice-matched triple-junction solar cells, PVSC 2015 Proceeding (2015).
[4] N. Baladés, M. Herrera, D.L. Sales, J. Pizarro, P. Galindo, M. González, S. Tomasulo, J. Abell, R. Walters, S.I. Molina, Structural characterization of InAlAsSb/InGaAs/InP for solar cells, Unplublished results.
[5] A.N. Semenov, V.A. Solov'ev, B.Y. Meltser, Y.V. Terent'ev, L.G. Prokopova, S.V. Ivanov, Molecular beam epitaxy of AlInAsSb alloys near the miscibility gap boundary, J. Cryst. Growth 278 (2005) 203–208.
[6] R.R. LaPierre, T. Okada, B.J. Robinson, D.A. Thompson, G.C. Weatherly, Lateral composition modulation in InGaAsP strained layers and quantum wells grown on (100) InP by gas source molecular beam epitaxy, J. Cryst. Growth 158 (1996) 6–14.
[7] L. Nieto, J.R.R. Bortoleto, M.A. Cotta, R. Magalhaes-Paniago, H.R. Gutierrez, Strain relaxation and stress-driven interdiffusion in InAs/InGaAs/InP nanowires, Appl. Phys. Lett. 91 (2007).
[8] M. Herrera, D. Gonzalez, M.U. Gonzalez, Y. Gonzalez, L. Gonzalez, R. Garcia, Composition modulation in low temperature growth of InGaAs/GaAs system: influence on plastic relaxation, Microchim. Acta. 145 (2004) 63–66.
[9] T.L. McDevitt, F.S. Turco, M.C. Tamargo, S. Mahajan, D.E. Laughlin, V.G. Keramidas, W.A. Bonner, Effects of substrate orientation on phase-separation in ingaas and ingaasp epitaxial layers, Inst. Phys. Conf. Ser. (1989) 173–180.
[10] A. Lahiri, Effect of epitaxial strain on phase separation in thin films, Arxiv_1310 5899 (2013) v1.
[11] R.F. Egerton, P. Li, M. Malac, Radiation damage in the TEM and SEM, Micron 35 (2004) 399–409.
[12] M. Gonzalez, M.P. Lumb, L.C. Hirst, Stephanie Tomasulo, Rapid thermal annealing of InAlAsSb lattice-Matched to InP for top cell applications, 43rd IEEE Photovoltaic Specialists Conference (PVSC) (2015).
[13] G.B. Stringfellow, Immiscibility and spinodal decomposition in III/V alloys, J. Cryst. Growth 65 (1983) 454–462.
[14] F. Peiro, A. Cornet, J.R. Morante, M. Beck, M.A. Py, Surface roughness in InGaAs channels of high electron mobility transistors depending on the growth temperature: strain induced or due to alloy decomposition, J. Appl. Phys. 83 (1998) 7537–7541.
[15] L.C. Hirst, M.P. Lumb, J. Abell, C.T. Ellis, J.G. Tischler, I. Vurgaftman, J.R. Meyer, R.J. Walters, M. Gonzalez, Spatially indirect radiative recombination in InAlAsSb grown lattice-matched to InP by molecular beam epitaxy, J. Appl. Phys. 117 (2015).
[16] T. Grieb, K. Mueller, E. Cadel, A. Beyer, M. Schowalter, E. Talbot, K. Volz, A. Rosenauer, Simultaneous quantification of indium and nitrogen concentration in InGaNAs using HAADF-STEM, Microsc. Microanal. 20 (2014) 1740–1752.
[17] L. Bellaiche, A. Zunger, Effects of atomic short-range order on the electronic and optical properties of GaAsN, GaInN, and GaInAs alloys, Phys. Rev. B 57 (1998) 4425–4431.

[18] W. Li, J. Turpeinen, P. Melanen, P. Savolainen, P. Uusimaa, M. Pessa, Effects of rapid thermal annealing on strain-compensated GaInNAs/GaAsP quantum well structures and lasers, Appl. Phys. Lett. 78 (2001) 91–92.

[19] Y.W. Zhao, Z.Y. Dong, Annihilation of deep level defects in InP through high temperature annealing, J. Phys. Chem. Solids 69 (2008) 551–554.

[20] K. Mukherjee, D.A. Beaton, T. Christian, E.J. Jones, K. Alberi, A. Mascarenhas, M.T. Bulsara, E.A. Fitzgerald, Growth, microstructure, and luminescent properties of direct-bandgap InAlP on relaxed InGaAs on GaAs substrates, J. Appl. Phys. 113 (2013).

[21] D.D. Perovic, G.C. Weatherly, D.C. Houghton, On the electron-diffraction contrast of coherently strained semiconductor layers, Philos. Mag. A 64 (1991) 1–28.

[22] J.C. Jiang, A.K. Schaper, Z. Spika, V. Stolz, Strain-induced modulation versus superlattice ordering in epitaxial (GaIn)P layers, Phys. Rev. B 62 (2000) 15826–15833.

[23] K. Mukherjee, A.G. Norman, A.J. Akey, T. Buonassisi, E.A. Fitzgerald, Spontaneous lateral phase separation of AlInP during thin film growth and its effect on luminescence, J. Appl. Phys. 118 (2015).

[24] C.E. Pastore, M. Gutierrez, D. Araujo, E. Rodriguez-Messmer, Quantification of InxGa1-xP composition modulation by nanometric scale HAADF simulations, Appl. Surf. Sci. 269 (2013) 138–142.

[25] T. Grieb, K. Müller, R. Fritz, M. Schowalter, N. Neugebohrn, N. Knaub, K. Volz, A. Rosenauer, Determination of the chemical composition of GaNAs using STEM HAADF imaging and STEM strain state analysis, Ultramicroscopy 117 (2012) 15–23.

[26] H. Kauko, T. Grieb, R. Bjørge, M. Schowalter, A. Munshi, H. Weman, A. Rosenauer, A. van Helvoort, Compositional characterization of GaAs/GaAsSb nanowires by quantitative HAADF-STEM, Micron 44 (2013) 254–260.

[27] S.I. Molina, D.L. Sales, P.L. Galindo, D. Fuster, Y. Gonzalez, B. Alen, L. Gonzalez, M. Varela, S.J. Pennycook, Column-by-column compositional mapping by Z-contrast imaging, Ultramicroscopy 109 (2009) 172–176.

[28] A. Sanchez, R. Beltran, T. Beanland, M. Ben, M. de la Pena, A. Walls, J. Taboada, S. Molina, Blocking of indium incorporation by antimony in III–V-Sb nanostructures, Nanotechnology 21 (2010) 145606.

[29] G. Duscher, R. Buczko, S.J. Pennycook, S.T. Pantelides, Core-hole effects on energy-loss near-edge structure, Ultramicroscopy 86 (2001) 355–362.

[30] S.I. Molina, M.P. Guerrero, P.L. Galindo, D.L. Sales, M. Varela, S.J. Pennycook, Calculation of integrated intensities in aberration-corrected Z-contrast images, J. Electron Microsc. 60 (2011) 29–33.

[31] M. Varela, S.D. Findlay, A.R. Lupini, H.M. Christen, A.Y. Borisevich, N. Dellby, O.L. Krivanek, P.D. Nellist, M.P. Oxley, L.J. Allen, S.J. Pennycook, Spectroscopic imaging of single atoms within a bulk solid, Phys. Rev. Lett. 92 (2004).

[32] M. Varela, A.R. Lupini, K. van Benthem, A.Y. Borisevich, M.F. Chisholm, N. Shibata, E. Abe, S.J. Pennycook, Materials characterization in the aberration-corrected scanning transmission electron microscope, Annu. Rev. Mater. Res. 35 (2005) 539–569.

[33] S.W. Wang, A.Y. Borisevich, S.N. Rashkeev, M.V. Glazoff, K. Sohlberg, S.J. Pennycook, S.T. Pantelides, Dopants adsorbed as single atoms prevent degradation of catalysts, Nat. Mater. 3 (2004) 143–146.