

Stoichiometry and absolute atomic concentration profiles obtained by combined Rutherford backscattering spectroscopy and secondary-ion mass spectroscopy: InAs nanocrystals in Si

H Karl¹, I Grosshans¹, A Wenzel¹, B Stritzker¹, R Claessen¹,
V N Strocov¹, G E Cirlin², V A Egorov², N K Polyakov²,
Yu B Samsonenko², D V Denisov³, V M Ustinov³ and Zh I Alferov³

¹ Universität Augsburg, D-86135 Augsburg, Germany

² Institute for Analytical Instrumentation, RAS, 198903 St Petersburg, Russia

³ Ioffe Physico-Technical Institute, 194021 St Petersburg, Russia

Received 7 July 2001, in final form 5 March 2002

Published 16 September 2002

Online at stacks.iop.org/Nano/13/631

Abstract

Rutherford backscattering spectroscopy (RBS) and secondary-ion mass spectroscopy (SIMS) were combined to achieve depth profiling calibrated in absolute atomic concentrations. This method was applied to InAs nanocrystals, grown by molecular beam epitaxy (MBE), buried in a Si matrix. By means of RBS, with its capability of accessing the buried layers, we determined the depth-integrated areal densities of As and In. These were used to calibrate the SIMS profiles with their high depth resolution and dynamic range in absolute atomic concentrations. This allowed us to identify, besides a well confined layer of stoichiometric InAs nanocrystals, significant diffusion of In and As into the Si matrix in despite of their larger atomic radii, and an excess of As due to its non-reactive deposition on Si from the excess As₄ flux during the MBE growth. On the basis of these findings, we suggest measures to optimize the MBE process for InAs/Si and similar systems.

1. Introduction

Nanocrystals have a large potential for application in modern microelectronics. For example, the formation of an atom-like discrete electronic spectrum in the confining potential of nanocrystals—quantum dots—can increase the light-emitting efficiency. Characterization of the nanocrystal systems is however a challenging task, because the nanocrystals are normally buried in a host matrix under a capping layer with a thickness of some tens of nanometres.

Rutherford backscattering spectroscopy (RBS) is able to reach buried atomic layers non-destructively and gives information on the stoichiometry and atomic concentrations $n = \frac{dN}{dV}$, where N is the number of atoms, in absolute units. However, this technique is limited in depth resolution and

dynamic range of the atomic concentrations. Complementary secondary-ion mass spectroscopy (SIMS) has a depth resolution of less than a nanometer and a dynamic range of more than five orders of magnitude, but it is not able to give absolute atomic concentrations due to uncertain sputtering cross-sections. We have overcome this drawback by combining RBS and SIMS: the RBS data on the depth-integrated (areal) atomic concentrations $\frac{dN}{dS} = \int_0^\infty n(x) dx$ are used to calibrate the high-resolution SIMS profiles in absolute atomic concentrations.

The combined RBS–SIMS method was applied to InAs nanocrystals grown by MBE in a Si matrix [1]. Such incorporation of nanocrystals with a direct band gap is promising for integration of optoelectronics into the widespread Si technology. The InAs/Si system is particularly interesting, because

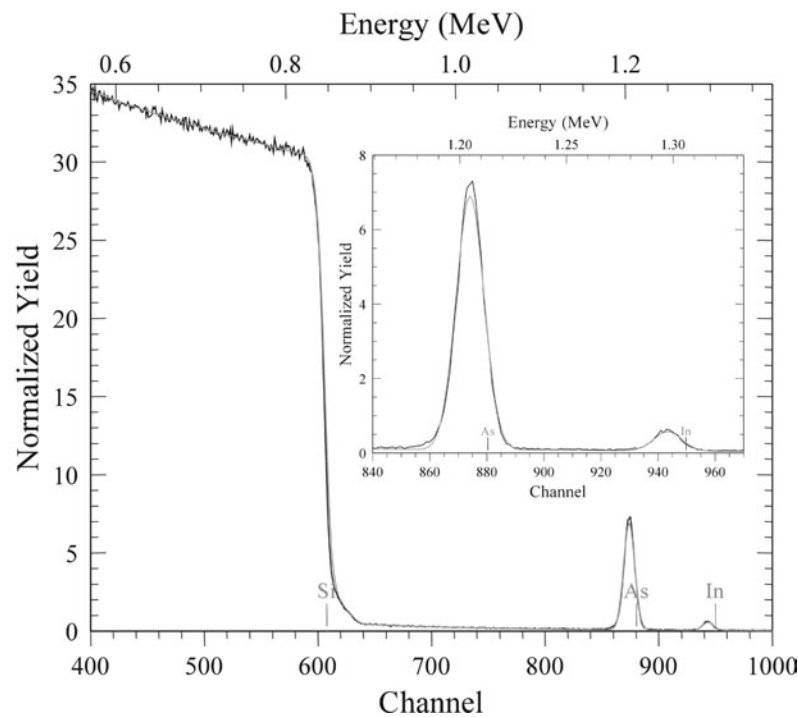


Figure 1. The RBS spectrum of InAs/Si sample *a* measured with the 1.5 MeV primary He⁺-ion beam. The steep increase in backscattering yield below 0.9 MeV is due to the Si matrix. The two peaks, also shown on an enlarged energy scale in the inset, are due to In and As. The areas below these peaks, weighted with the backscattering cross-sections, give the areal density of the corresponding atoms. The grey curve shows the fit used in RUMP [9] for the evaluation of the depth distributions.

the strain, induced by the lattice mismatch between InAs and Si, is presumably crucial to the formation of the type-I band alignment promoting an accumulation of electrons and holes in the nanocrystals and thus effective light emission.

Our experimental results on stoichiometry and absolute atomic concentration profiles $n(x)$ in a few InAs/Si samples reveal that this system is highly susceptible to interdiffusion of different elements during the MBE growth and annealing. In particular, despite their larger ionic radii, the In and As atoms easily leak into the Si matrix, which can change the band alignment on the InAs/Si interface. These findings suggest measures for further optimization of the growth process for InAs/Si and similar systems.

2. Experimental details

The InAs/Si samples were grown on oriented Si(100) substrates using an EP1203 (Russia) MBE machine. Thermal desorption of native silicon oxide was achieved by heating the substrate to $\sim 850^\circ\text{C}$ for 15 min. Well resolved (2×1) surface reconstruction, typical for clean Si(100) surfaces, was observed. At $\sim 650^\circ\text{C}$ a thick Si buffer layer was then deposited. After cooling down, the InAs layer was deposited at a rate of ~ 0.1 monolayers (ML) per second. The calibration of the growth rate and monitoring of the surface morphology during growth employed a reflection high-energy electron diffraction (RHEED) data acquisition system. As revealed by STM on similar samples [2], the as-grown InAs nanocrystals are pyramids with lateral dimensions of $12 \times 20 \text{ nm}^2$ and height of 4 nm. They are placed randomly and cover $\sim 50\%$ of the surface. The InAs layer grown was immediately covered by a

10–20 nm thick Si capping layer. The two samples investigated (*a* and *b*) differed somewhat in the InAs layer thickness (2 ML and 2.2 ML), deposition temperature (350 and 400°C), capping layer deposition time (180 and 60 min) and temperature (350 and 450°C). Moreover, sample *a* was annealed for 10 min at 700°C to activate migration of the surface atoms to smooth the resulting Si surface, while sample *b* was instead covered for 120 min at 700°C with an additional capping layer. The thermal budgets of the two samples, determined by the total deposition plus annealing time and temperature, were nevertheless close. The samples grown were characterized by photoluminescence (PL) spectroscopy, which revealed spectral peaks originating from the InAs nanocrystals [3].

The RBS measurements were performed with a TANDETRON accelerator. The energy of the He⁺-ion beam was chosen as 1.5 MeV, which allowed us to probe to depths much greater than the capping layer thickness, but was low enough to preserve sufficient depth resolution. The detector was located at 170°C relative to the beam direction.

The SIMS depth profiles were measured with an ATOMIKA 4100 system. The In⁺ profiles were measured by sputtering with the 5 keV O₂⁺ ions, and the As⁻, SiAs⁻ and O⁻ profiles with 5 keV Cs⁺ ions. We included the SiAs⁻ profiles because of an abundance of oxygen found: the ⁷⁵As signal might interfere with that of ²⁹Si³⁰Si¹⁶O. The size of the sputtering crater was $200 \times 200 \mu\text{m}^2$ in all cases.

3. Results

An RBS spectrum measured for sample *a*, which was grown under typical MBE growth conditions, is shown in figure 1.

It gives the energy spectrum of the backscattered He⁺ ions, where the energies can be rendered to depths based on known backscattering cross-sections (proportional to Z^2) and atomic densities. The spectrum shows well separated peaks of As and In. The steep increase in the backscattering yield at lower energies is due to the Si matrix. Its 'foot' towards higher energies relative to the Si position indicated is due to some pile-up in the detecting system and Si isotopes with higher masses. No traces of other elements were seen in the RBS spectrum.

The ratio of the areas below the As and In peaks, weighted with the corresponding backscattering cross-sections, directly gives the $\frac{N_{As}}{N_{In}}$ ratio of the total number of As atoms to that of In atoms. Surprisingly, $\frac{N_{As}}{N_{In}}$ was 29 ± 0.5 , indicating an enormous excess of As. Since the InAs nanocrystals have the ideal stoichiometry, as indicated by high-resolution TEM [4], the excess As atoms must be diluted in the Si capping layer and substrate.

The absolute areal concentrations, required for calibration of the SIMS profiles, were found on the basis of the known backscattering cross-sections using the standard software RUMP [5]. We have obtained $\frac{dN_{As}}{ds} = (7.0 \pm 0.3) \times 10^{15} \text{ cm}^{-2}$ and $\frac{dN_{In}}{ds} = (0.24 \pm 0.01) \times 10^{15} \text{ cm}^{-2}$. The error bars were estimated by evaluation of the RBS spectra measured with different He⁺-ion beam energies between 1.45 and 1.55 MeV (the errors of each single fit were much smaller). To assess the As and In depth distributions, we used RUMP to fit the spectrum. The distributions were modelled by single Gaussian profiles with adjustable position and width, which was a reasonable assumption since the estimated depth resolution of RBS did not exceed 10 nm. We have found the maxima of the As and In depth distributions, both at 15.0 ± 0.6 nm.

SIMS depth profiles measured on the same sample *a* are shown in figure 2. Independent determination of the depth scale was achieved by measuring the depth of the sputtered crater using a stylus depth profiler. The profiles of In and, to a lesser extent, As decay exponentially towards the surface and substrate, which justifies the assumption of a Gaussian concentration profile in the RBS data analysis. To calibrate the In and As profiles in the absolute atomic concentrations n_{As} and n_{In} , as shown in figure 2, we integrated the experimental profiles $p_{In,As}(x)$ over the depth and equated these figures to the areal densities found by RBS: $A \int_0^\infty p_{In,As}(x) dx = \frac{dN_{In,As}}{ds}$, where A determines the calibration as $n_{In,As}(x) = A p_{In,As}(x)$. This calibration now enables a direct comparison of the absolute distributions of In and As measured with high depth resolution and dynamic range typical of SIMS. Note that the $^{16}\text{O}^-$ profile, also shown in figure 2, could not be calibrated (the oxygen signal was not seen in the RBS spectrum) and cannot be directly compared with the In and As profiles. In any case, the total oxygen concentration, being below the RBS detection limit, is insignificant compared to In and As.

The SIMS profiles within a depth smaller than ~ 2 nm are strongly influenced by surface effects due to non-stationary sputtering conditions and a native silicon dioxide layer formed during storage in air. This can be seen in a rapid fall of the $^{16}\text{O}^-$ signal within the first 4 nm. At the depth of ~ 20 nm this signal rises however to a maximum placed deeper than the In and As maxima. This indicates a buried oxygen layer probably due to residual oxygen at the substrate surface below

the Si buffer layer. Interference of the signal from ^{75}As with that from $^{29}\text{Si}^{30}\text{Si}^{16}\text{O}$ is manifested by a notable peak in the corresponding profile just near the surface (~ 2 nm).

For the sample *b* the experimental results were similar. However, the $\frac{N_{As}}{N_{In}}$ ratio of 15.5 ± 1 indicated smaller excess of As. The areal densities were found to be $\frac{dN_{As}}{ds} = (0.5 \pm 0.1) \times 10^{15} \text{ cm}^{-2}$ and $\frac{dN_{In}}{ds} = (0.047 \pm 0.03) \times 10^{15} \text{ cm}^{-2}$. The As profile had an additional prominent maximum at the depth of ~ 12 nm, indicating significant enrichment of the surface region in As. The $^{16}\text{O}^-$ signal gradually decreased towards greater depth without any sign of the buried oxygen layer. A systematic analysis of the atomic concentration profiles and their connection with the MBE growth conditions for a series of InAs/Si samples will be published elsewhere.

4. Discussion

Analysis of the In and As absolute atomic concentration distributions reveals interesting peculiarities of our InAs/Si systems:

- (1) The SIMS profiles $n_{In,As}(x)$ in figure 2 show that the In and As concentrations do not drop sharply beyond the InAs layer but decay exponentially (linearly in the logarithmic plot of figure 2). This identifies significant diffusion of In and As into the Si capping layer and substrate, promoted by elevated temperatures during the MBE growth and annealing. Upon passing the InAs layer the observed decay may in principle have extrinsic contributions: first, the sputtering ions, by knock-on collisions, can drive atoms further into the sample (ion beam mixing); second, the sputtered atoms can redeposit onto the surface. To discriminate against these effects, we measured SIMS profiles with low-energy Cs⁺ ions (1 keV) which reduced both ion beam mixing and redeposition. The profiles remained unchanged. This confirms that the experimental profiles reflect the true diffusion of In and As atoms into the Si matrix.
- (2) Comparison of $n_{In}(x)$ with $n_{As}(x)$ shows that As is in excess through the whole sample. This holds even in the region of the InAs layer. As the high-resolution TEM results [4] indicate that the InAs nanocrystals themselves have the ideal stoichiometry, the excess As atoms in this layer are distributed at very high concentration in the Si matrix between the InAs nanocrystals. In the capping layer the excess of As is larger than that in the substrate, as $n_{As}(x)$ decays towards the surface much more slowly than $n_{In}(x)$. This indicates that the As atoms appeared in this region due, apart from diffusion, to capture of As atoms during growth of the capping layer: it was grown immediately after the growth of the InAs layer, while the As₄ partial pressure decreases rather slowly after closing the shutter.

The observed accumulation of In and particularly As in the Si matrix can significantly influence the light emission efficiency of the InAs nanocrystals: acting as dopants to Si, these impurities can change the band alignment at the InAs/Si interface. In principle, the excessive As doping, similarly to the strain, shifts the bands in Si towards the type-I alignment required for the carrier accumulation and can therefore increase the light emission efficiency.

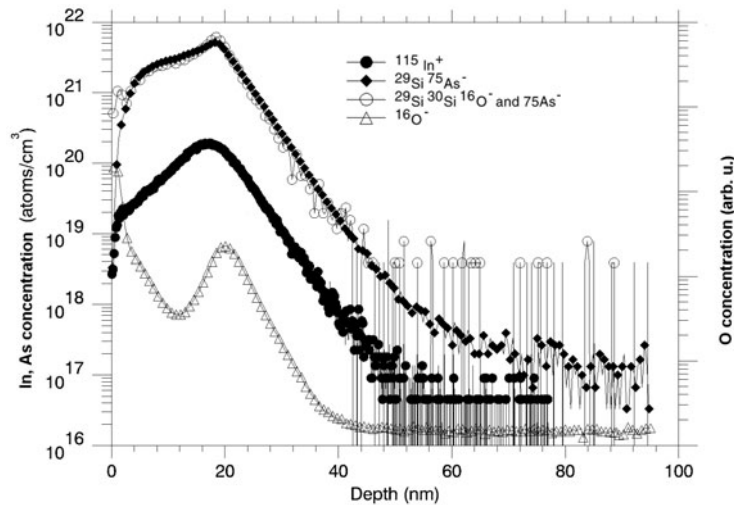


Figure 2. SIMS depth profiles of the InAs/Si sample *a* measured with 5 keV sputtering ions O_2^+ (the $^{115}In^+$ profile) and Cs^+ (the $^{28}Si^{75}As^-$, $^{29}Si^{30}Si^{16}O^-$ and $^{75}As^-$ profiles). The In and As profiles are calibrated in absolute atomic concentrations using the RBS data, while the O profile is not calibrated. The concentration profiles show significant diffusion of the In and As atoms into the Si matrix, excess of As through the whole sample and accumulation of As in the capping layer.

Our findings have practical implications, suggesting measures for optimizing the MBE growth of InAs/Si and similar systems if reduction of the In and As concentrations in the Si matrix is required:

- (1) Usually, diffusion of In and As into Si is considered negligible due to the ionic radius of In and As being larger than that of Si. Our results demonstrate that the diffusion is in fact significant. To reduce this effect, lower temperatures should be used during the MBE growth and annealing.
- (2) The MBE growth of InAs is usually carried out in an excess of As_4 flux. This implies that As atoms, by analogy with the growth of the III–V semiconductors, can deposit on the surface only if reacted with In atoms. Our observation of the enormous excess of As demonstrates that its atoms can in fact easily deposit on Si without In. Therefore, the flux of As_4 should be chosen approximately stoichiometric with that of In. Moreover, the As concentration enhancement in the Si capping layer suggests that before deposition of this layer after the InAs growth, a pause should be introduced sufficient for reduction of the As_4 background pressure, followed by flashing off of the adsorbed As atoms.

5. Conclusions

We have demonstrated a combined RBS–SIMS method, in which the absolute areal atomic densities $\frac{dN}{dS}$, determined by RBS with its capability for accessing non-destructively the buried layers, are used to calibrate the SIMS depth profiles, characterized by high depth resolution and dynamic range, in absolute atomic concentrations n . This method was applied to MBE-grown InAs nanocrystals buried in Si. The absolute concentration profiles determined, $n_{In}(x)$ and $n_{As}(x)$, have given a wealth of previously obscured information about this system. Besides a well confined layer of stoichiometric InAs nanocrystals, we have found significant diffusion of In and As

atoms into the Si matrix, promoted by elevated temperatures during the MBE growth and annealing, despite their larger atomic radii. These atoms, acting as dopants, can influence the band alignment at the InAs/Si interface and therefore the light emission efficiency of the InAs nanocrystals. We have also found enormous excess of As over In throughout the whole sample, which is due to non-reactive deposition of As onto the Si surface from an excessive As_4 flux. On the basis of these findings, we have suggested measures for optimizing the MBE process for InAs/Si and similar systems: reduction of the growth and annealing temperatures; use of a As_4 flux stoichiometric to that of In; and introducing a pause before growth of the capping layer sufficient for reduction of the As_4 background pressure.

Acknowledgments

The financial support by the Alexander von Humboldt Foundation (G E Cirlin) and the INTAS Young Scientists Programme (V A Egorov) is gratefully acknowledged.

References

- [1] Cirlin G E, Petrov V N, Dubrovskii V G, Masalov S A, Golubok A O, Komyak N I, Ledentsov N N, Alferov Zh I and Bimberg D 1998 *Tech. Phys. Lett.* **24** 290
- [2] Cirlin G E, Dubrovskii V G, Petrov V N, Polyakov N K, Korneeva N P, Demidov V N, Golubok A O, Masalov S A, Kurochkin D V, Gorbenko O M, Komyak N I, Ustinov V M, Egorov A Yu, Kovsh A R, Maximov M V, Tsatsul'nikov A F, Volovik B V, Zhukov A E, Kop'ev P S, Alferov Zh I, Ledentsov N N, Grundmann M and Bimberg D 1998 *Semicond. Sci. Technol.* **13** 1262
- [3] Heitz R, Ledentsov N N, Bimberg D, Egorov A Yu, Maximov M V, Ustinov V M, Zhukov A E, Alferov Zh I, Cirlin G E, Soshnikov I P, Zakharov N D, Werner P and Gösele U 1999 *Appl. Phys. Lett.* **74** 1701
- [4] Zakharov N D, Werner P, Gösele U, Heitz R, Bimberg D, Ledentsov N N, Ustinov V M, Volovik B V, Alferov Zh I, Polyakov N K, Petrov V N, Egorov V A and Cirlin G E 2000 *Appl. Phys. Lett.* **76** 2677
- [5] Doolittle L R 1986 *Nucl. Instrum. Methods B* **15** 227