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Enhanced In surface segregation during molecular-beam epitaxy of (In,Ga)As on (h11) GaAs for small values of h

Matthias Ilg
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70506 Stuttgart, Germany

Klaus H. Ploog
Paul-Drude-Institut fur Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

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We present a systematic study of indium surface segregation during molecular-beam epitaxy of (In,Ga)As on (h11) GaAs. Ultrathin InAs monolayer structures serve as segregation probes and are investigated by high-resolution x-ray diffraction and photoluminescence spectroscopy. An envelope-function analysis of the photoluminescence data reveals a strong enhancement of In segregation on the GaAs (111), (211), and (311) surfaces with respect to their (100) counterpart. Reflection high-energy electron-diffraction measurements confirm this observation, which is of fundamental importance for the understanding of non-(100)-oriented semiconductor heterostructures.

Surface segregation effects represent the ultimate veto of nature against the crystal grower's quest for total control on an atomic scale. Therefore, during the past years, intense investigations in the field of semiconductor heterostructures (SH) have focused on this phenomenon[1-6] because the atomic configuration of the interfaces crucially influences the structural and electronic properties of these engineered crystals. It is the molecular-beam epitaxy (MBE) of $In_xGa_{1-x}As/GaAs$ structures which has gained the status of a model system and for which now rich and detailed information is available. However, only sparse data exist on the influence of the growth axis on the segregation process. Such information is a prerequisite for the understanding of non-(100)-SH's with their interesting and novel properties, such as built-in piezoelectric fields[7] and interface corrugations.[8] Investigations of segregation in metal alloys show the importance of the surface orientation,[9] and the recent study of a (311)-InAs/GaAs sample[10] suggests that the same could be true for semiconductors. In this paper we present a systematic study of In surface segregation effects during MBE of (In,Ga)As on GaAs surfaces of the important (h11) family. In particular we consider the cases $h=1$, 2, 3, and ∞, i.e., GaAs substrates with (111), (211), (311), and (100) orientation. As segregation probe we use ultrathin InAs quantum wells, which show a strong dependence of the quantized levels on segregation effects. High-resolution double-crystal x-ray diffraction (HRDXD) confirms the structural integrity of our samples which then are investigated by photoluminescence (PL) spectroscopy. A numerical analysis of the PL results as well as reflection high-energy electron diffraction (RHEED) as a second, independent method reveal enhanced In segregation for all the investigated non-(100) orientations. Finally, we discuss the consequences of the thus resulting structural inequivalence between nominally identical heterostructures with different orientations.

We use conventional solid-source MBE to synthesize our structures on (100), (311), (211), and (111) GaAs substrates, which are soldered side by side with In on a Mo holder. The growth process is monitored *in situ* by means of RHEED. First a GaAs buffer layer of 0.2 μm thickness is grown at a substrate temperature of 620 °C. Three InAs wells of 3 Å thickness[11] separated by 530-Å-thick GaAs barriers are grown with a rate of 0.2 Å/s at 380 °C, 430 °C, and 480 °C. Since an increase of the substrate temperature activates the segregation process[2,4] we are thus able to study different segregation profiles within the same sample. HRDXD is performed with a double diffractometer in Bragg geometry using a 12-kW generator with a copper target as x-ray source. The diffraction patterns are recorded in the vicinity of the symmetrical GaAs (333), (422), (311), and (400) reflections. For the PL experiments the samples are mounted in an optical cryostat at 6 K and excited by the 647.1-nm line of a Kr^+ laser. The emitted light is focused on the entrance slit of a 1-m single-grating monochromator and detected by a liquid-nitrogen-cooled Ge detector. The spectral resolution of the PL setup is better than 0.5 meV.

Before we delve into the optical properties we first present in Fig. 1 the HRDXD spectra of our samples. The agreement between experimental and theoretical[12] patterns is excellent for the (100), (311), and (211) structures. Only in the (111) case we see some deviations, which, however, at least partially are due to the pathological character of the low-intensity GaAs(333) reflection. We emphasize at this point that although HRDXD is an extremely valuable tool to assess such properties as interface smoothness and strain status, it clearly is—at least for this specific set of sample parameters—not very sensitive to segregation effects. Indeed, for the experimental data presented in Fig. 1 we can provide an excellent fit assuming three identical InAs wells with ideally sharp interfaces, although the PL measurements presented below reveal the distinct character of each of the three wells. An introduction of a smeared In profile influences the outcome of the simulations only insignificantly. But the agreement between simulated and experimental x-ray patterns shows the structural excellence of our samples which—apart from segregation—do not deviate from the intended structure.

Having gained this reassuring knowledge, we now in-

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vestigate the optical properties. The PL spectra presented in Fig. 2 were taken at a high excitation density of 30 W/cm^2 (Ref. 13) in order to screen out the internal electric fields of the (311), (211), and (111) samples.[14] In this way we facilitate the numerical analysis presented below which can be carried out under the assumption of an internal field of strength zero. The segregation of In has two important consequences. It blueshifts the PL peak,[15] and, as it washes out the quantum-well potential, it tends to narrow the PL linewidth.[16] In our experiments we observe a separation of the PL peaks ranging from 23 meV in the (100) to a striking 50 meV in the (111) case. This shift brings the peaks of the 480 °C wells of the different orientations very close together and wipes out the individual character still present for the quantum wells grown at lower temperature. In a similar way the linewidths for the 480 °C wells are quite similar while stronger differences are present for the 380 °C and 430 °C wells. We note that the observed linewidths compare very favorably to the literature values of up to 22 meV for InAs/GaAs heterostructures.[17]

In order to extract the In segregation profiles from the observed PL peak positions we carry out a numerical analysis of the PL data. We carry out a finite potential-well calculation within the envelope-function model requesting continuity of wave functions and probability currents at the interfaces.[18] Due to the fact that the carriers bound to these ultrathin InAs wells spend less than 10% of their time actually inside the wells, the InAs heavy-hole and electron masses as well as band nonparabolicities[16,19] only insignificantly influence the positions of the energy levels. These positions essentially hinge on three parameters, namely, the strained InAs heavy-hole gap, the band-offset ratio $Q_c^{(h11)}$, and the carrier masses in GaAs. The hh gap is calculated using the formalism of Van de Walle[20] for the (100) and (111) structures and interpolated between these two extremes for the [311] and [211] directions. The ratios between (100) and non-(100) heavy-hole masses are taken from Xia.[21,22] Our choice for the GaAs (h11) masses is well in the middle of the range of values stated in the literature,[23,24] and even with the somewhat smaller values given elsewhere, the con-

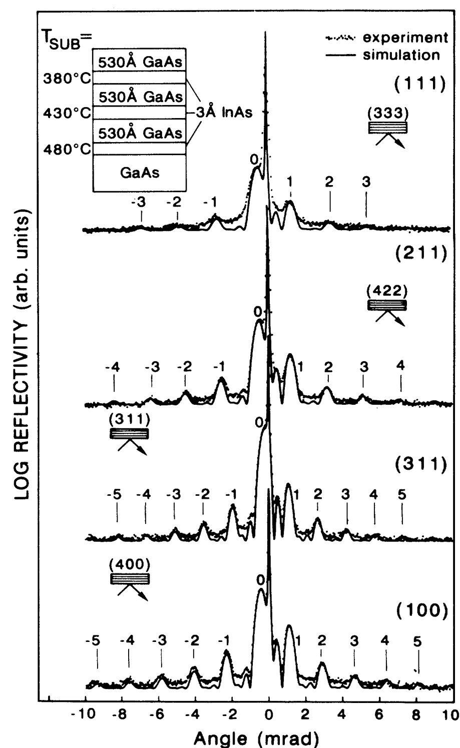

FIG. 1. Experimental and simulated x-ray diffraction patterns of the (h11) samples taken in the vicinity of the symmetrical (333), (422), (311), and (400) GaAs reflections. Each sample contains three InAs quantum-well structures grown at different substrate temperatures. The simulation was carried out assuming three identical quantum wells with abrupt compositional profiles.

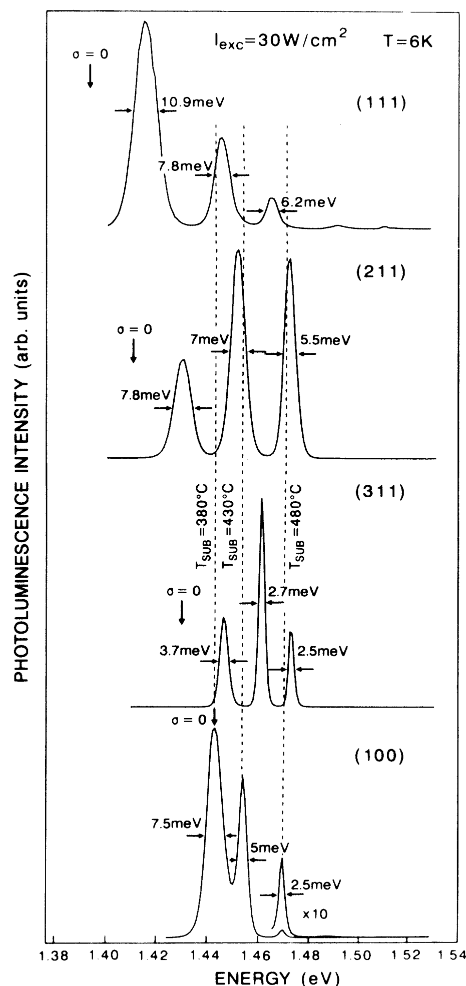

FIG. 2. PL spectra of the same set of samples taken at 6 K. Arrows indicate the PL energy predicted in the absence of segregation (segregation probability $\sigma=0$). The valence-band anisotropy shifts these transitions to the red for the non-(100) orientations. Even though the PL peaks of the (211) and (111) samples tend to be lower in energy than the (100) and (311) peaks, segregation effects are more pronounced along these directions because of the larger discrepancy between theoretically predicted and experimentally observed transitions.

clusions presented below are sound. Hirakawa *et al.*[25] propose a value of 0.4 for $Q_c^{(100)}$, which is supported by a recent PL study of an InAs/GaAs sample for which the In concentration profile is explicitly known from x-ray standing wave (XSW) experiments.[26] For small In concentrations the value of $Q_c^{(100)}$ is 0.6 (Ref. 4) and therefore we interpolate $Q_c^{(100)}$ between these extremes. For the other orientations no experimental values of $Q_c^{(h11)}$ exist. From the solid-on-solid model by Van de Walle[20] we deduce a tendency for the non-(100) values to be smaller than $Q_c^{(100)}$. Therefore, we clearly do not overestimate the In segregation length in non-(100) structures if we assume $Q_c^{(h11)}=0.4$ for all h.

The In segregation profile is described by the standard model[4,5] assuming a probability σ for In atoms to switch their position with arriving Ga atoms during overgrowth. This model yields the expression $x_n=(1-\sigma)\sigma^{n-1}$ for the In content x_n of the $(n-1)$th layer of the GaAs cap with $n=1$ corresponding to the original plane of InAs deposition. This segregation probability σ is converted into a segregation length λ via the equation $\lambda=-d_{h11}/\ln\sigma$, where d_{h11} stands for the $(h11)$-lattice plane separation.[27] Due to In atoms on positions not directly below the surface during the arrival of the first GaAs atoms, i.e., on positions below the subsurface, in the (311) and (211) samples[11] it is unlikely that all In atoms participate with the same probability σ in the segregation process along these directions. We rather expect the topmost In atoms to participate with a higher probability than the In atoms buried underneath. Because we do not know the ratio of these probabilities we carry out calculations for two extreme models. The first model assumes segregation of all In atoms irrespective of their initial positions, whereas in the second one only the topmost In atoms, i.e., the subsurface In atoms, segregate. The first model yields a lower and the second one an upper bound to the segregation length.

In Fig. 3 we present the results of our calculations. We cannot explain the (211) data by assuming segregation of subsurface atoms only because even a σ of 1 does not produce a high enough PL energy for the 480 °C well. Only with all In atoms participating in the segregation process can we fit the data. This result is in clear contrast to previous findings, for example, in the (100)-Si/Ge system.[28] Furthermore, even assuming a participation of all In atoms in the segregation process with the same probability, we see for the two high-index orientations (211) and (311) as well as for the singular (111) surface a much larger segregation length than for the (100) case.

In order to support this conclusion, we now present the results of an independent determination of the segregation length using the elegant RHEED method suggested by Gerard.[29] This method detects *in situ* surface-segregated In by monitoring the transition from two-dimensional (2D) to 3D growth of an InAs layer grown on top of the investigated structure. However, contrary to the original work, we think that this procedure does not yield the actual amount of In present on the surface but an upper limit, because it is not clear to which extent subsurface In atoms can participate in the islanding process. Nevertheless, this method gives a measure of the In

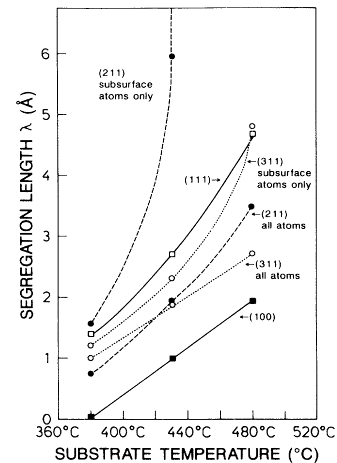

FIG. 3. In segregation lengths as calculated from the PL data. For (211) and (311) samples two different calculations were carried out assuming participation of all deposited In atoms in the segregation process and participation of only subsurface In atoms. Lines are guides to the eye.

segregation tendency and thus allows us to compare different substrate orientations. In our case a comparison is only possible for (211), (311), and (100) samples, because InAs does not exhibit 3D growth on the (111) surface.[30] Experiments were carried out under conditions identical to those during synthesis of the PL sample. The results displayed in Fig. 4 contain two important pieces of information. First, the resulting segregation lengths are so strongly inflated in comparison to the PL results that only a dramatic change of the band-structure data employed in the calculations could bring the two data sets into agreement. Because the PL data are backed by an XSW investigation,[26] we conclude that the RHEED method used here clearly does not yield but an upper limit to the actual In composition of the surface. But secondly, they provide the desired confirmation of the In segregation enhancement deduced from the PL experiments. Also the (211) segregation lengths are systemati-

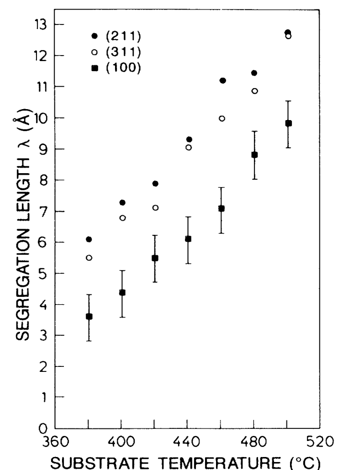

FIG. 4. Segregation lengths as derived from RHEED experiments.

cally larger than the (311) values, and therefore we can give—combining RHEED and PL results—the following order of segregation lengths: $\lambda_{(111)} > \lambda_{(211)} > \lambda_{(311)} > \lambda_{(100)}$.

What is the driving force behind this phenomenon? Meléndez *et al.*[10] observe the ground state of their (311) sample synthesized by atomic-layer molecular-beam epitaxy (ALMBE) 26 meV above that of the (100) sample whereas in our case this difference is never larger than a few meV. Therefore, the In segregation in their (311) sample is much more enhanced with respect to the (100) reference than in our case. This observation implies that the key role is played by the surface tension, because ALMBE brings about surface reconstructions different from those of conventional MBE, whereas other energetic contributions, such as interface and strain energies, are identical during MBE and ALMBE. And indeed, RHEED experiments show that InAs deposition on GaAs (311), (211), and (111) surfaces[31,32] always has a beneficial influence on the surface quality, in contrast to GaAs (100) where an InAs coverage results in a more diffuse RHEED pattern. This observation indicates an anisotropy in the difference in surface tensions between InAs-covered and clean GaAs ($h11$) surfaces, and it is not unreasonable to assume this anisotropy to be the driving force behind the In segregation enhancement described in this work.

The observed strongly anisotropic behavior of In segregation implies that the simultaneous synthesis of (In,Ga)As/GaAs heterostructures on variously oriented substrates creates different segregation lengths and thus *inequivalent and not directly comparable* structures. Therefore the widely used approach to the investigation of non-(100) SH's via comparative studies of (100) and non-(100) samples grown side by side leads to erroneous conclusions, and should be viewed with caution unless the anisotropy of In segregation is taken into account. Furthermore, it shows that modulated-temperature[33,34] and predeposition techniques[6] designed to circumvent segregation effects cannot be simultaneously successful on (100) and non-(100) substrates. These statements not only hold for the (In,Ga)As/GaAs system and the substrate orientations discussed here, but certainly are valid also for other orientations and combinations of materials.

In conclusion we have investigated In surface segregation effects during MBE on GaAs ($h11$) surfaces using PL and RHEED investigations of InAs monolayer structures. Both methods independently show an enhanced tendency of In segregation on the non-(100) surfaces. Combining RHEED and PL measurements we show the segregation lengths to increase in the following order: $\lambda_{(100)} < \lambda_{(311)} < \lambda_{(211)} < \lambda_{(111)}$.

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