Influence of growth direction on order-disorder transition in $(GaAs)_{1-x}(Si_2)_x$ alloys

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$(GaAs)_{1-x}(Si_2)_x$ metastable alloys were epitaxially grown on (001), (111), (110), and (112) GaAs. Single-crystal alloys were obtained for Si concentrations in the range $0 \leqslant x \leqslant 0.43$. At higher concentrations the Si segregated. The long-range order parameter, for each growth direction studied, was determined as a function of Si concentration by high-resolution x-ray diffraction. The behavior of this parameter with Si concentration is influenced by growth direction. This fact provides direct evidence that the substrate geometry affects the atomic ordering of these alloys. The results obtained from these alloys provide additional support to the validity of the proposal that the growth direction influences the order-disorder transition observed in other alloys of this kind.

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Several compounds of the $(III\text{-}V)_{1-x}(IV_2)_x$ metastable alloys have been widely studied, due to their potential of tailoring the properties of III-V semiconductors, which may be useful for device applications.[1–5] Moreover, these alloys have been grown as model systems to study order disorder transitions,[1–5] where an ordered phase is associated to the zinc blende structure (III-V-like) and a disordered phase is associated to the diamond structure (IV-like). This order disorder transition exists at some intermediate value x_c when IV atoms are increased in concentration from $x=0$ to $x=1$.[1–5]

We have recently proved that the order disorder transition in $(GaAs)_{1-x}(Ge_2)_x$ metastable alloys is influenced by growth direction and that the atomic ordering in these alloys is ruled mainly by the substrate geometry.[6,7] Our results ruled out the applicability of the thermodynamic models to our experimental data, since none of them predicted any different critical concentration for samples grown on differently oriented substrates. On the other hand, a model of the growth process based on Monte Carlo simulations gave results in good agreement with the experimentally observed long-range order (LRO) in $(GaAs)_{1-x}(Ge_2)_x$ alloys, for all the studied growth directions. In our previous work,[6,7] we stated that quite likely the growth direction might affect the order disorder transition of similar $(III\text{-}V)_{1-x}(IV_2)_x$ alloys, since when grown on (001) oriented substrates, different metastable alloys $(GaAs)_{1-x}(Ge_2)_x$,[1,5] $(GaSb)_{1-x}(Ge_2)_x$,[2] and $(GaAs)_{1-x}(Si_2)_x$ (Ref. 4) have a similar critical concentration $x_c(001) \approx 0.3$ of the IV element. The growth of $(III\text{-}V)_{1-x}(IV_2)_x$ metastable alloys, other than $(GaAs)_{1-x}(Ge_2)_x$, would give insight on the generality of our previous result, and the applicability of the growth model to other alloys of this kind. In addition, $(GaAs)_{1-x}(Si_2)_x$ alloys may find applications as buffer layers for the growth of GaAs on Si. Undesirable effects induced by the large lattice mismatch between GaAs and Si may be reduced by growing a $(GaAs)_{1-x}(Si_2)_x$ buffer layer of a graded Si concentration. On the other hand, the possible application of these alloys in semiconductor laser technology has been demonstrated by Burnham *et al.*[8]

In this paper we report the observation of the influence of growth direction on the long-range order disorder transition in $(GaAs)_{1-x}(Si_2)_x$ alloys with $0 \leqslant x \leqslant 0.43$ epitaxially grown on (001), (111), (110), and (112) GaAs. At higher concentrations the Si segregated and single-crystal alloys could not be obtained. The LRO parameter, experimentally determined by high-resolution x-ray diffraction (HRXRD) has a dependence on the substrate orientation, evidencing that the growth direction affects the atomic ordering of these alloys. The experimental results are compared with those of a growth model, based on Monte Carlo simulations, for $(III\text{-}V)_{1-x}(IV_2)_x$ metastable alloys, that has been previously described.[7,9]

$(GaAs)_{1-x}(Si_2)_x$ metastable alloys were epitaxially grown on (001), (111), (112), and (110) GaAs, in a rf planar magnetron sputtering system with a base pressure better than 10^{-7} mbar. Growth conditions and system characteristics are given in Ref. 10.

All samples were measured by high-resolution x-ray diffraction in a MRD Philips diffractometer. All measurements were carried out in the (220) configuration of a Ge-four crystals Bartels monochromator. The rocking curves were least square fitted to Gaussian line shapes, in order to determine the integrated intensities, peak positions and the full widths at half maximum (FWHM).

During the growth experiments, it was not possible to obtain single-crystal metastable alloys for Si concentrations over 0.43. The growth of alloys with concentrations higher than this value, resulted either in polycrystalline alloys or layers where Si segregated, as indicated by Raman scattering experiments.[10] As the difference in growth temperature to obtain polycrystalline films (570 °C) or segregation (580 °C) is relatively small, we were not able to control the experimental conditions to determine if single crystal alloys can be obtained in this small temperature window.

The Si concentration of the alloys was determined from HRXRD, using both symmetrical and asymmetrical reflections and considering the linear behavior with Si concentration of the alloy bulk lattice parameter that has been previously reported for these alloys.[4] The long-range order parameter was determined following previously reported procedures.[2,7] For $(III\text{-}V)_{1-x}(IV_2)_x$ alloys the LRO parameter can be taken as $S=(1-2f)$,[2,7] where f is an antisite

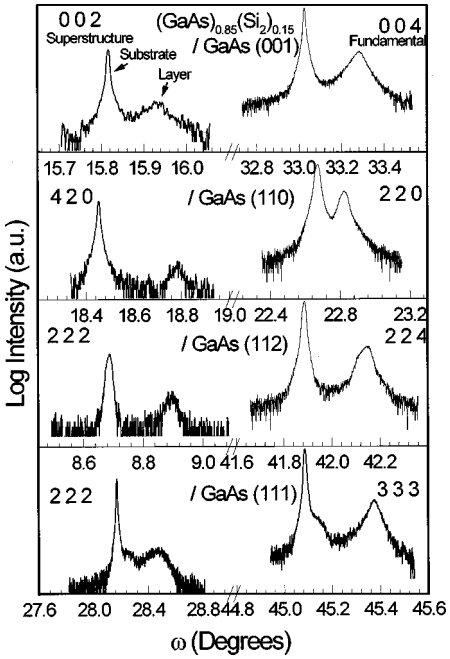

FIG. 1. Typical diffraction profiles of fundamental and superstructure reflections obtained by HRXRD for $(GaAs)_{0.85}(Si_2)_{0.15}$ metastable alloys epitaxially grown on (a) (001), (b) (110), (c) (112), and (d) (111) GaAs.

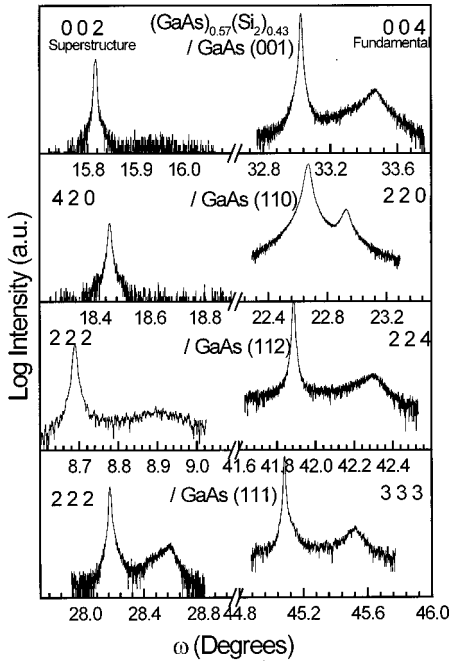

FIG. 2. Fundamental and superstructure reflections rocking curves of $(GaAs)_{0.57}(Si_2)_{0.43}$ epitaxially grown on (a) (001), (b) (110), (c) (112), and (d) (111) GaAs.

fraction, that indicates the amount of Ga (As) atoms that are in the As (Ga) sites, with respect to the substrate. This *f*, takes values from zero (zinc blende structure) to 0.5 (diamond structure). Different reflections are required to evaluate this parameter, those reflections allowed for both zinc blende and diamond structures are called fundamental, while a superstructure reflection is only exhibited by a zinc blende crystal.[2] Evaluating the atomic scattering factors of Ga, As, and Si at the diffraction angle of each of the studied reflections, for the four crystalline orientations we take the LRO parameter, for $(GaAs)_{1-x}(Si_2)_x$ alloys as

$$S \cong \frac{(1-0.62x)}{(1-x)} R^{1/2},$$

where R is the ratio of the superstructure to fundamental reflection integrated intensities of the alloy, normalized to those of the substrate, and it is obtained from the rocking curves.[2,7]

Typical diffraction profiles for the grown samples are shown in Figs. 1 and 2. The substrate and layer peaks are clearly observed in these figures. The layer peaks are broadened mainly because of the layer thickness and the dislocations generated during the lattice relaxation process. From the FWHM corrected for layer thickness,[11] the dislocation density in the layers were found to be in the range from 1×10^7 to 3×10^8 cm^{-2}.

Superstructure and fundamental reflections for alloys with $x = 0.15$ are presented in Fig. 1 for each of the studied growth directions. Since the superstructure reflection of the alloys is observed for the four crystalline orientations, at this Si concentration all the layers have the zinc blende structure. On the other hand, it can be seen in Fig. 2, that when Si concentration is increased to $x = 0.43$, the superstructure peak associated with the alloy has vanished for (001) and (110) grown alloys, i.e., alloys grown with these orientations suffer a zinc blende to diamond transition. However, (112) and (111) grown $(GaAs)_{1-x}(Si_2)_x$ alloys did not exhibit any order disorder transition up to this Si maximum concentration obtained. The superstructure reflection (222) shown by the (112) and (111) grown alloys evidences that these alloys still have the zinc blende structure, therefore the critical concentrations for these orientations should be higher than $x = 0.43$.

The shoulder observed in the rocking curves for the samples grown on GaAs(111) is produced by the formation of an interfacial layer of low Si concentration. We confirmed this affirmation from SIMS measurements where two layers with different Si concentration are observed, the thicker upper layer corresponds to a Si concentration of 0.15 and the innermost to a concentration around 0.01. The origin of this layer may be due to cross contamination during GaAs buffer layer growth.

The LRO parameter behavior with Si concentration for the studied crystalline orientations is shown in Fig. 3. The symbols represent the experimental data obtained from the rocking curves, while the solid and dashed lines show the modeled long-range order parameter. The growth model used for the simulations has been previously described.[7,9] Full squares in Fig. 3(a) give the order parameter for (001) grown samples, which is in good agreement with previously reported data for this alloy. The critical concentration is $x_{cSi}(001) = 0.37 \pm 0.04$, which is obtained from a least square fit between a quadratic curve to the experimental data, the critical concentration is determined setting the fitting func-

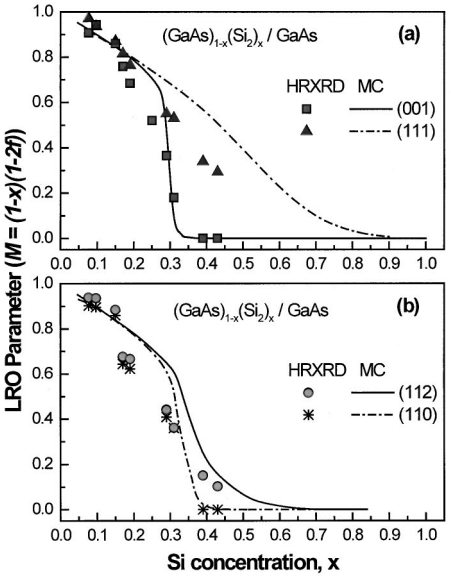

FIG. 3. Experimental and modeled long-range order parameter behavior with Si concentration of $(GaAs)_{1-x}(Si_2)_x$ epitaxially grown on (a) (001) and (111) and (b) (110) and (112) GaAs.

tion equal to zero. The overall uncertainty in the critical concentration is derived from the fit described above and the procedure used to determine the alloy concentration. From a comparison between the concentrations determined by HRXRD and SIMS the uncertainty in the values obtained from x-ray diffraction is estimated to be at most $\Delta x = 0.03$ for the full range of concentrations. The value obtained for the critical concentration for this growth direction is in good agreement with that obtained from differential reflectance spectroscopy $x_c(001) \approx 0.34$,[12] and with previously reported results for other $(III\text{-}V)_{1-x}(IV_2)_x$ metastable alloys also obtained by HRXRD, $x_c(001) \approx 0.36$ for $(GaAs)_{1-x}(Ge_2)_x$ (Ref. 5) and $x_c(001) \geqslant 0.30$ for $(GaSb)_{1-x}(Ge_2)_x$.[2]

Full triangles, also shown in this figure, give the order parameter behavior for (111) grown layers. It is clear that growth direction influences the atomic ordering of $(GaAs)_{1-x}(Si_2)_x$ alloys, so a different long-range order is obtained from samples of the same Si concentration, grown under the same conditions, but on top of differently oriented substrates. However, as we were not able to grow samples with Si concentrations over $x = 0.43$, it is not possible to know experimentally the critical concentration associated with this growth direction, or if $(GaAs)_{1-x}(Si_2)_x$ (111) grown layers do not suffer a zinc blende to diamond transition as it is predicted by the growth model and it is experimentally observed in the previously reported $(GaAs)_{1-x}(Ge_2)_x$ (111) alloys.[6,7]

For (112) grown layers, the order parameter is shown in Fig. 3(b) with full circles. As it can be seen from the behavior of the LRO parameter with Si concentration, the alloys grown with this orientation do not present an order-disorder transition in the compositional range $0 \leqslant x \leqslant 0.43$. The critical concentration for this orientation, expected to be higher than 0.43, is out of reach from the present set of experimental data. No comparison is possible for this substrate orientation with that predicted by the model $x_{cMC}(112) = 0.65$, or with that experimentally obtained for $(GaAs)_{1-x}(Ge_2)_x$ alloys $x_{cGe}(112) \approx 0.59$.[6,7] In Table I all critical concentrations x_c obtained from simulation and x-ray experiments are shown.

TABLE I. Comparison between critical concentrations of Si at which the zinc blende to diamond transition occurs in $(GaAs)_{1-x}(Si_2)_x$.

Growth direction	Fundamental reflection	Superstructure reflection	x_c (HRXRD)	x_c (MC)
(001)	004	002	0.37 ± 0.04	0.33
(110)	440	442	0.39 ± 0.04	0.40
(112)	224	222	>0.43	0.65
(111)	444	222	>0.43	1.0

The comparison of the experimental and modeled order parameters shows that for (001) grown alloys there is a satisfactory agreement. However, for the other growth directions there are some systematic differences between the experimental and theoretically determined LRO parameters. The experimental data seems to fall more abruptly than the modeled parameters. Several factors such as vacancies, As deficiency, and the preferential substitution of Si in one of the sublattices (Ga or As) where incorporated in the growth model[7,9] with the aim to understand the behavior of the LRO parameter for these growth directions. None of these factors by itself produces significant effects on the modeled parameters to explain the observed deviations. On the other hand, when all kind of atomic bonds, including the so-called ''wrong'' pairs Ga-Ga and As-As are allowed in the growth model, the agreement between experimental and modeled parameters seems to improve at midrange Si concentrations, mainly for the (111) grown samples, however, we have not any additional evidence of possible ''wrong'' pairs present in any concentration in these alloys.

In conclusion, $(GaAs)_{1-x}(Si_2)_x$ metastable alloys with $0 \leqslant x \leqslant 0.43$ have been grown on (001), (111), (110), and (112) GaAs by rf magnetron sputtering. The behavior of the long-range order parameter with Si concentration, experimentally determined by HRXRD, is influenced by growth direction. These results provide direct evidence that the atomic ordering of $(GaAs)_{1-x}(Si_2)_x$ alloys is influenced by the substrate geometry and that this phenomena is observed independently of the IV column element.

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