X-ray photoelectron-diffraction study of intermixing and morphology at the Ge/Si(001) and Ge/Sb/Si(001) interface

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We used the XPD (x-ray photoelectron diffraction) and AED (Auger electron diffraction) from Ge core levels to probe the crystalline structure of 3 and 6 ML of Ge epitaxially grown by molecular-beam epitaxy on the Si(001) surface. In order to check the film tetragonal distortion and the pseudomorphic growth morphology, we used two different temperatures of the substrate during the deposition: room temperature and 400 °C. Evidence for an interfacial intermixing has been found by means of the observation of the angular behavior of the intensity of the emitted electrons. We also investigated the effects of Sb as a surfactant on such an interface. In this case indications of a laminar growth of strained Ge overlayer with reduced intermixing is obtained when 1 ML of Sb is predeposited on the substrate. Furthermore making use of a multiple-scattering approach to reproduce the experimental XPD patterns, a higher amount of accessible information on the morphology of the interface, beyond the determination of the strain content, is obtained. [S0163-1829(96)05436-7]

I. INTRODUCTION

An XPD (x-ray photoelectron diffraction) pattern represents the modulations of the measured photocurrent, usually from a core level, as a function of the kinetic energy and/or the emission direction of the analyzed photoelectrons. As is well known, modulations occur as the result of the interference between the primary photoelectronic wave and the portions of this wave elastically scattered by the atoms surrounding the photoabsorber. Their study, therefore, provides local structural information around the emitter atom.[1,2] At high photoelectron energies ($E_{\mathrm{kin}} \geqslant 500$ eV) these patterns can be easily interpreted in terms of forward scattering along directions connecting neighbor atoms to the emitter,[2] and very often a simple single scattering analysis corroborates such an approach. This atomistic picture, naturally linked with the chemical sensitivity of the photoemission experiment, can easily provide an accurate tool to investigate the strain relief and intermixing of the overlayers growth in the epitaxial mode.[3,4]

We used such a tool to revisit the growth of Ge on Si(001),[4] in the scenario proposed by the total-energy calculation[5] and electron microscopy investigations,[6] which suggest the existence of a sizable degree of intermixing during the growth and/or subsequent annealing of Si/Ge heterostructures. To date the role played by the intermixing has not been properly clarified in terms of strain content and surface morphology, and in our opinion it deserves a deeper investigation. In particular it has not shown the role of the intermixed phase at the transition for three-dimensional (3D) islands formation, in the so called Stranski-Krastanov[7] growth mode. Intermixing has been clearly found in the case of Ge segregation on the Si/Ge(001) interface,[8] and it is generally supposed to have an activation temperature of the order of 300 °C, even if evidence of Ge segregation at deposition temperatures as low as 50 °C has been reported from analysis of core-level photoemission peaks.[9]

More debated is the problem of the Ge/Si(001) surface, which is supposed to be sharper in character. Surface-extended x-ray-absorption fine structure measurements have detected exchange mechanisms between Si and Ge after the second layer of Ge is deposited,[10] while medium-energy ions scattering[11] results suggest some degree of intermixing only after 3 ML of Ge deposition at 500 °C on the Si(001). On the other hand, Sasaki *et al.*[12] reported about deep interdiffusion of Ge in Si even after 1 ML of Sb-mediated deposition. Finally, no indication of Ge interdiffusion at room temperature (RT) deposition has been reported so far.

To know how sharp the interface is is crucial in the field of next generation optoelectronic devices,[13] because, after observation of a quasidirect transition due to the electronic band zone folding in Si/Ge superlattices (SL's),[14] all theoretical calculations were based on strained Si/Ge SL's with sharp interfaces.[15] Aiming at clarifying this topic, a dynamical analysis of diffraction patterns of electrons emitted from this interface is reported in order to obtain quantitative results of this first stage of interface formation and the dependence on temperature of such a formation. We focus our research on the critical thickness for island nucleation on the surface, by studying the deposition range between 3 and 6 ML. In the present investigation values of the tetragonal distortion close to those expected on the basis of the theory of elasticity are found. Nevertheless contributions to the strain amount, in the presence of relaxation channels such as island formation, have been determined.

After a brief description of the apparatus (Sec. II) and of the method used (Sec. III), we report a study of 3 and 6 ML Ge/Si(001) interfaces grown by molecular-beam epitaxy (MBE), in the two cases of RT and 400 °C of the substrate (Sec. IV). In Sec. V a similar study is performed for the case of Sb-mediated growth of the Ge/Si(001) interface. The conclusions are reported in Sec. VI.

II. EXPERIMENT

The samples used in the present experiment were MBE grown in a Riber SIVA 32 apparatus equipped with three

Knudsen cells for Ge, Si, and Sb evaporation. The base pressure of the MBE chamber at room temperature was always lower than 5.0×10^{-11} torr. The error bar on temperature control was better than 1 °C for both the evaporation cells and the substrate as was measured by their own thermocouple. The substrate were well-oriented Si(001) wafers, *p*-doped (5/10 Ω cm). Cleaning of the silicon surface was based on two stages: (i) an *ex situ* chemical etching based on a simplified Shiraki procedure, and (ii) an *in situ* desorption of the native oxide by heating the wafer up to 840 °C in the presence of an atomic flux of silicon directed onto the surface until a sharp double domain 2x1-reconstructed Si(001) surface was observed by reflection high-energy electron diffraction (RHEED). A liquid nitrogen shroud allows the base pressure of the chamber (5×10^{-11} torr) not to rise above 8×10^{-11} torr during evaporation and sample heating. Ge evaporation at the rate of 0.72 ML/min has been monitored by means of RHEED oscillations and beam equivalent pressure calibration. The RHEED apparatus is equipped with a 10 kV *e*-gun and an eight-bit camera used to record patterns on the phosphorescent screen with a sensitivity of 0.5 lux. The angle of incidence of the electron beam during the present experiment was about 0.6°. The experimental chamber is also equipped with an x-ray Al K_α source and a Riber MacII electron analyzer converted to an angle-resolved one by reducing the angular acceptance to ($6°\times6°$) by screening 354/360° of the full circular aperture. A sample manipulator allows the rotation of the sample in azimuth and polar angle mode with an accuracy of 0.1° during XPD pattern acquisitions.

III. METHODOLOGY

The main task we want to accomplish in this paper is to show how XPD, a largely accessible technique to many x-ray photoelectron spectroscopy users, can be succesfully used to retrieve nondestructive and *in situ* information relative to the growth morphology of thin epitaxial layers. As a matter of fact, the use of XPD has very often been limited at the level of submonolayer deposition, and very seldom have quantitative determinations been carried out for thicker overlayers or clean surfaces.[2,3]

A refined analysis of experimental data requires the consideration of several problems relative to the calculation of XPD patterns.[2] All these effects[16,17] complicate the simplified picture of the forward-scattering approximation, very often used in the case of energetic electrons ($\geqslant$500 eV). That is (i) cluster convergence, (ii) use of a realistic value of the mean free path, and (iii) effects induced by multiple scattering. In particular a theoretical problem is represented by the convergence in the number of atoms needed to reproduce the observed photoemission intensity. In the past a substantial discrepancy has been found in the comparison of the experimental data with a single-scattering theory for clusters whose dimensions were comparable to the estimated value of the electron mean free path in the solid. This is probably due to the greater complexity of the process underlying the loss of coherence of the primary photoelectron wave. A more realistic picture could be approached by introducing defocusing effects, first discussed by Poon and Tong,[17] which affect diffraction along rows of atoms in the crystal. The introduction

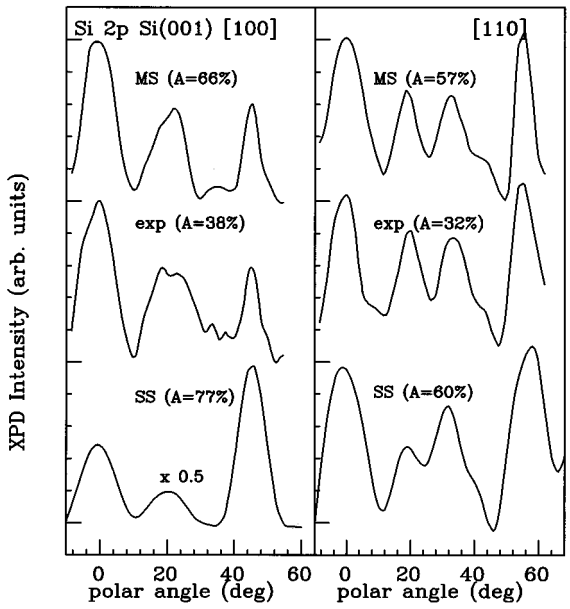

FIG. 1. Comparison with experiment after fully converged multiple scattering (MS) calculation (12 planes, third scattering) of a Si(001) surface and the relative approximation by a single-scattering (SS) event. The calculations are referred to polar angle Si 2*p* XPD along the [100] and [110] directions. Values of the anisotropy for the experimental and theoretical curves are reported.

of additional scattering events proved to be crucial in obtaining cluster convergence at ''physical'' sizes and good comparison with the experiment. Very recently a similar breakdown of single-scattering analysis was shown by Chen *et al.*[18]

The calculation apparatus has been tested with the case of clean double-domain Si(001)-2×1 surface, which is the starting point of all the experiments reported in this paper. All the calculations are based on a scattering matrix method derived by Rehr and Albers,[19] and recently applied by Agliz, Quémerais, and Sébilleau.[20] This method replaces the plane-wave scattering factor by scattering matrices that account for the spherical character of the incoming and outgoing photoelectron waves. We set the dimension of these matrices up to 6, which, as we checked by increasing this value, leads to results almost indistinguishable from the full spherical wave calculation. Due to the pronounced peaking of the scattering factor in the forward direction, we may neglect all multiple-scattering pathways with scattering angles larger than 30°. Complex phase shifts have been calculated up to an $l_{\max}$ value of 23 by means of a Hedin-Lundqvist (HL) potential as recently applied to x-ray-absorption study.[21] We found that contribution from 12 Si planes is able to reproduce the Si 2*p* XPD polar patterns measured along the two main polar scans [100] and [110]. This corresponds to a mean free path in the solid of the order 15–20 Å traveled by electrons having a kinetic energy of 1100–1400 eV and a number of atoms in the cluster of the order of 500–700. For clusters of this size a dominant contribution to the cross section due to events of scattering up to third order has been found, in agreement with the overall picture provided by Kaduwela, Friedmann, and Fadley.[22] This approximation will be kept hereafter in the paper. In Fig. 1 we report a comparison be-

tween the experimental data, the single-scattering calculations, and the multiple-scattering (MS) calculations. The theoretical data are normalized to the experimental ones. Values of the relative anisotropies are reported as well. Angular patterns have been taken along [100] and [110] directions, for emission of Si 2*p* electrons excited by Al $K\alpha$ photons (1486 eV). Experimental values of the anisotropy are very close to those of a similar study performed by Kubler *et al.* [23] It can be observed that only multiple scattering is able to reproduce correctly both the intensity and the width of characteristic features of the patterns. Henceforth, to better rely on a quantitative analysis of the structural and morphological properties of the Ge strained overlayer grown on Si(001), we shall make use of such a MS approach.

IV. GROWTH OF Ge/Si(001)

Ge/Si(001) is generally considered to follow a Stranski-Krastanov (SK) growth mode, i.e., a layer by layer mode followed by a 3D island growth[7]. As pointed out by Le-Goues, Copel, and Tromp[24] and Matthews and Blakeslee,[25] on the basis of elastic theory, Si substrates cannot provide enough dislocations to relax strain energy. As a consequence, the growth of coherent islands is the preferred mechanism to relax strain. For this reason, the theory of elasticity establishes only a lower value for the estimate of the ''limit thickness.'' Other authors have reported that the limit thickness of the overlayer varies from 2 and 11 ML.[26]

Actually there are two other aspects which can be considered in assessing the growth mode: morphology and intermixing. The first one is an additional way to relax strain energy by introduction of missing atoms rows, while the latter has been found to reduce principally the total energy of the film.[5] In both cases these two mechanisms could combine in providing different limit thicknesses. Eaglesham and Cerullo[27] reported the appearance of coherent islands strained to the substrate. The formation of coherent islands on the continuous layer induces a strain field in the substrate, with a partial relaxation of the strain. Only in a later stage dislocations appear in the film.

The most established picture of the Ge/Si(001) interface formation, having sufficient kinetics on the surface ($T \geqslant 400$ °C),[26] is represented by a three-step process: (1) At the very beginning a laminar film of Ge, of 2–3 ML, grows epitaxially and strained on the Si substrate. (2) Between 3 and 6 ML of deposited Ge, several experiments[26,28,29] have shown the constitution of islands by the presence of a range of limited variation in the measured quantity. (3) Beyond 6 ML, evidence of a ball up of Ge, which leads to coalescence of islands with thousands of Ge atoms and generation of some bare Si areas, are reported. Conversely, during deposition at RT, the Ge atoms tend to occupy the most probable positions available on the surface without forming three-dimensional islands.

In Fig. 2 we report the time behavior of a line scan parallel to the sample surface taken from phosphorescent screen image of RHEED patterns. The incident beam was along direction [110] of the Si substrate, during Ge deposition at 400 °C. As can be seen, only after the formation of the third layer is a progressive increase of the in-plane lattice parameter observed. This transition accompanies the strong damping in the RHEED oscillation intensity, as reported in Fig. 3, not expected in the case of layer-by-layer growth. After 6-ML equivalent Ge deposition, the in-plane lattice parameter resulted to be about 2% greater than that of the Si substrate. Also at this time, a sudden change in the RHEED pattern is observed with the appearance of spots which indicate a transition to a 3D growth mode. The proposed interface after such a preparation is described by a Ge epitaxial layer of thickness ranging between 2 and 4 ML with dispersed large islands, as shown by transmission electron microscopy.[24,27] A sudden increase in the island height at about 6-ML coverage has also been observed from x-ray reflection data.[30]

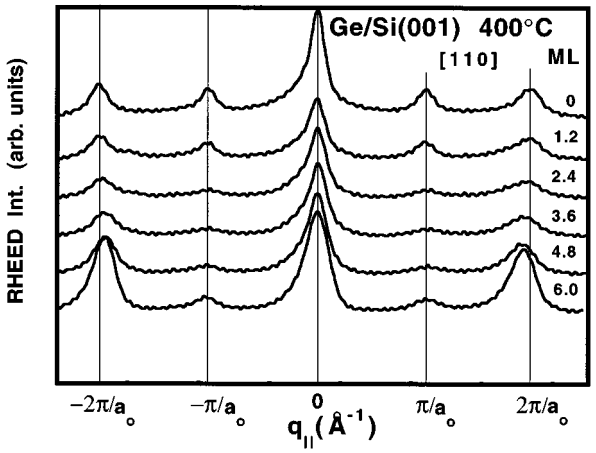

FIG. 2. RHEED pattern during 6 ML Ge deposition on Si(001) at 400 °C. The curves are line scans of the intensity on the phosphor screen taken parallel to the shadow edge, and showing the (± 1) and $(\pm \frac{1}{2})$ order of the zeroth-order Laue zone. The electron beam was incident along the [110] direction.

Recent observations of sizable intermixing,[10,12] at the early stages of interface formation, suggested that we reconsider in detail the growth mechanism which hampers the sharp interface formation. We intend to use XPD to study the amount of Ge interdiffusion in the Ge/Si(001) interface. To this end we will pay particular attention in the discrimination of effects due to roughness and/or island formation from the mechanism of interface constitution. In Fig. 4 we report re-

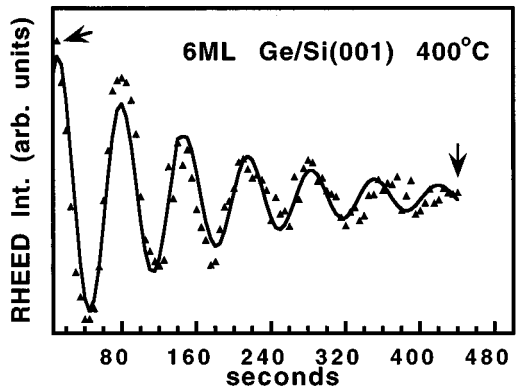

FIG. 3. Intensity oscillations of RHEED central spot during 6-ML Ge/Si(001) deposition at 400 °C. The arrows indicates the opening and closing of the shutter. A value of the period of the oscillations of about 83 s has been found.

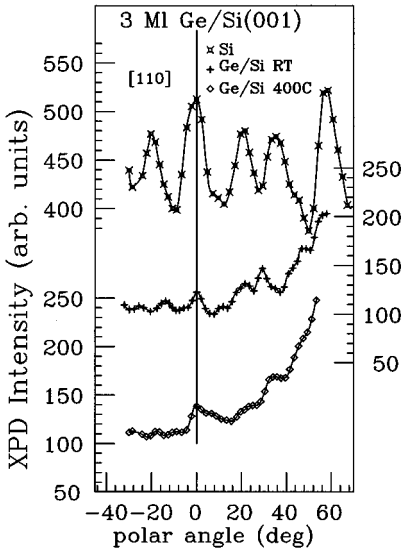

FIG. 4. XPD from clean Si $2p$ 2×1-Si(001) surface (top curve) compared with anisotropy of emission of Ge $3d$ electrons from 3-ML Ge deposition on the 2×1-Si(001) substrate taken at room temperature (middle curve) or with the substrate kept at 400 °C (bottom curve). The normal emission is emphasized by the vertical line.

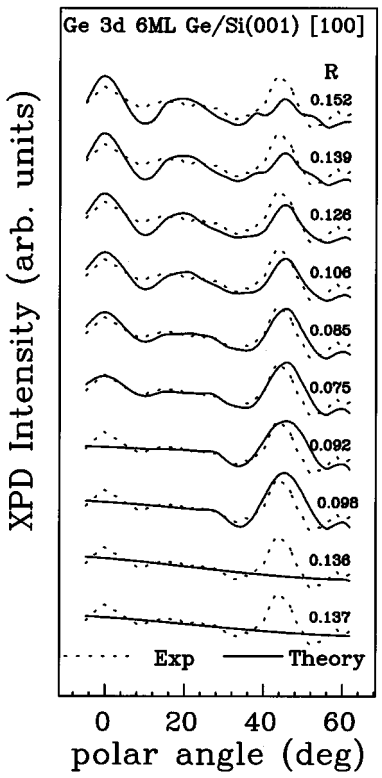

FIG. 5. The solid lines represent theoretical Ge $3d$ XPD features obtained as a function of the increased number of Ge unstrained planes. Each normalized theoretical curve is directly compared to the experiment for 6-ML Ge/Si(001) deposited at 400 °C (dashed line), performed along the [100] direction. The level of agreement between calculation and experiment is shown by the value of the R-factor.

sults of a Ge $3d$ XPD experiment from 3 ML Ge deposited at RT (middle curve) and at 400 °C (bottom curve). The measurements were collected along the [110] direction, and compared to the value of the anisotropy of the clean Si $2p$ XPD (top curve). We note that the peak corresponding to a 0° polar angle (normal emission) is present for both temperatures used during the Ge deposition. This is a hint of an interdiffusion process at the interface. Indeed, this peak can be caused only by electrons emitted by deep Ge atoms forward scattered by atoms located at least four planes below the surface. Actually, the presence of the 2×1 reconstruction destroys these paths, making necessary the existence of at least 6 ML-thick Ge or Si-Ge overlayers. Particularly at RT this observation is difficult to explain in terms of a sizable roughness.

To assess the occurrence of sizable intermixing at the interface, we also show the results of an experiment done with 6-ML-equivalent deposition of Ge at 400 °C. In fact the higher value of the Ge photoemission signal results, in this case, in a smaller error in the standard data reduction procedure, for the determination of the value of the area of the core-level peak of interest. The error on the area has been estimated to be of the order of 3%, resulting, in the scale of the anisotropy, in an error bar ranging from 10% to 15% for the experiments reported in this work.

In Fig. 5 we present a comparison of the experiment done along the [100] direction with a calculation of a plane-by-plane contribution of 10 ML of unstrained Ge. This kind of comparison allows us to follow in detail the growth of the heterostructures through the successive evolution of the features of the XPD pattern. The level of agreement between theory and experiment is quantified by the value of the R factor, defined as the sum of absolute values of the differences between theory and experiment, normalized by the number of experimental points. The theoretical curves are normalized to the experimental ones. Figure 6 shows the same comparison referred to the [110] direction. As can be seen, for both directions, the relative value of the intensity of the features strongly resembles the experimental XPD contribution as built up with five layers of Ge atoms. Actually if we want to introduce the reconstruction, this fifth layer corresponds to the sixth one. The reconstruction of the top Ge layer has been introduced by a simple symmetric dimer model.[10] As in the experiment performed by Chambers and Loebs,[4] we measured the tetragonal distortion content of the Ge overlayer from the angular displacement of the Ge $3d$ photoemission peak along the [101] direction, corresponding to 45° polar angle in the [100] polar pattern. In Fig. 7 we report the best fits between experiment and theory for the XPD patterns taken along both emission directions of 6 ML of Ge on Si(001). A tetragonal distorted out-of-plane lattice parameter (5.75 ± 0.02 Å) is found, 6% greater than the Si lattice parameter (5.43 Å). This tetragonal deformation corresponds to the same perpendicular elongation found by Chambers and Loebs[4] of the XPD peak located at 45° polar emission, in the hypothesis of conservation of the Si in-plane lattice parameter. We stress that the single scattering model used by the above authors in the determination of the strain was the suitable one because of the thinner film thickness (4 ML) under study. For such a very thin layer, the contribution

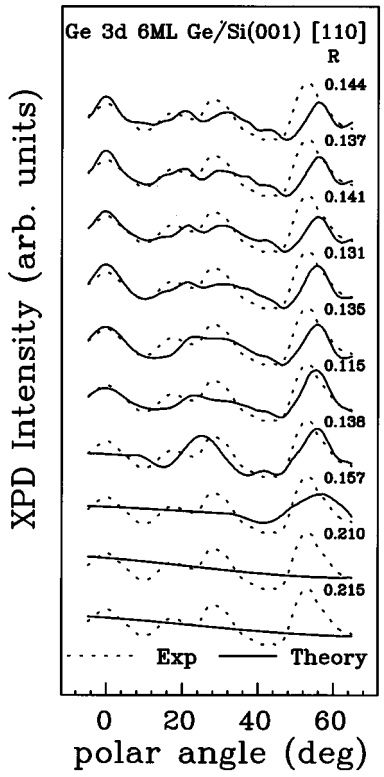

FIG. 6. Same as Fig. 5, taken along the [110] direction.

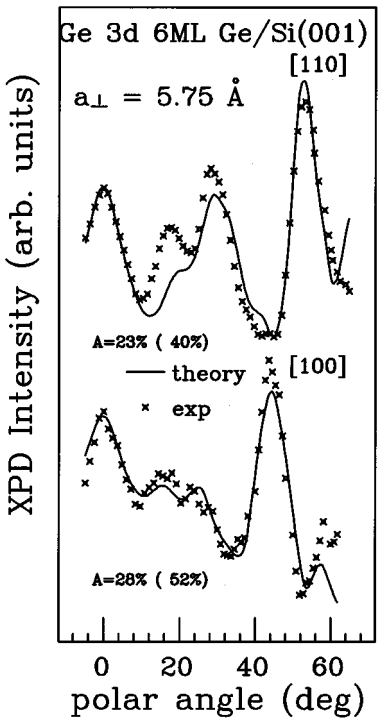

FIG. 7. Best-fit comparison between theory and experiment for the case of XPD of the Ge 3*d* core level from 6 ML of Ge deposited on the 2×1-Si(001) substrate kept at 400 °C. The emission direction is along the [110] (top curves) and along the [100] (bottom curves). A value of 5.75 ± 0.02 Å for the out-of-plane lattice parameter in the Ge overlayer is obtained. The value of the in-plane lattice parameter is 5.43 Å. Values of the XPD anisotropy for the experimental and theoretical curves are reported.

to the XPD pattern is mainly due to the single scattering of photoelectrons.

In the following, in the determination of the tetragonal elongation, we will always refer to a Si in-plane lattice parameter. The evolution of a relaxation of such an in-plane lattice parameter, as we have observed by RHEED, involves, in fact, the most superficial Ge layers without modifying the initial setup of the pseudomorphic growth. The value of 5.75 ± 0.02 Å obtained is lower by about 0.08 Å than the value calculated from the theory of elasticity. From this theory the perpendicular lattice parameter can be calculated from the Ge bulk stiffness constants C_{12} and C_{11}, Ge lattice parameter a_{Ge}, and Si lattice parameter $a_{\parallel}$ by the equation

$$a_{\perp}/a_{\parallel}-1\approx\epsilon_{\perp}-\epsilon_{\parallel}=-\epsilon_{\parallel}(1+2C_{12}/C_{11}), \qquad (1)$$

where $\epsilon_{\parallel}=a_{\parallel}/a_{\mathrm{Ge}}-1$ or equivalently $a_{\perp}=(1+\epsilon_{\perp})a_{\mathrm{Ge}}$. $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the in-plane and out-of-plane component of the symmetrical strain tensor respectively. Results from classical theory have been favorably compared with the local-density-functional calculation,[31] and this lower value of strain content can be put in relation with strain relief mechanisms occurring at the interface.

Same analyses have been applied to XPD curves reported by Diani *et al.*[32] for 6 ML of Ge, deposited at 400 °C and at RT, on a vicinal surface cut 4° off the [110] direction. Polar patterns are taken along the [110] surface.[32] Figure 8 reports the XPD data of Diani *et al.* fitted with our theoretical approach. In this case a sizable difference between the out-of-plane lattice parameters ($a_{\perp}$) has been found for the two temperatures of the experiments. At 400 °C the value of $a_{\perp}=5.75\pm0.02$ Å is found in complete agreement with our experiment, while at RT deposition a value of 5.82 ± 0.02 Å is obtained.

Moreover the best fit of the Diani *et al.*'s RT experiment has been obtained with nine planes of scatterers. This means that to build up all features needed to reproduce the XPD patterns, a larger number of layers compared to that of a nominal thickness is necessary. These results suggest that an important interdiffusion process occurs even at room temperature.

V. Sb-MODIFIED GROWTH OF Ge/Si(001)

Recently the use of surfactants, in particular As and Sb, which segregate to the surface, resulted to be extremely important in preventing island formation and intermixing during the growth performed at high temperatures (500–700 °C) (Refs. 28, 33, and 34) necessary to improve the photoluminescence properties of the film.[35]

During Sb-assisted growth deposition, the clean Si(001) surface was kept at a temperature ranging between 500 and 700 °C, while a partial pressure of Sb of the order of 10^{-7} torr from the Sb Knudsen cell was directed toward the sample. A short annealing at 600 °C was used to get rid of Sb in excess of about 1 ML on the 2×1-Sb/Si(001) surface observed by RHEED. XPS profiles confirmed the presence of about 1 ML of Sb when compared with the photoemission

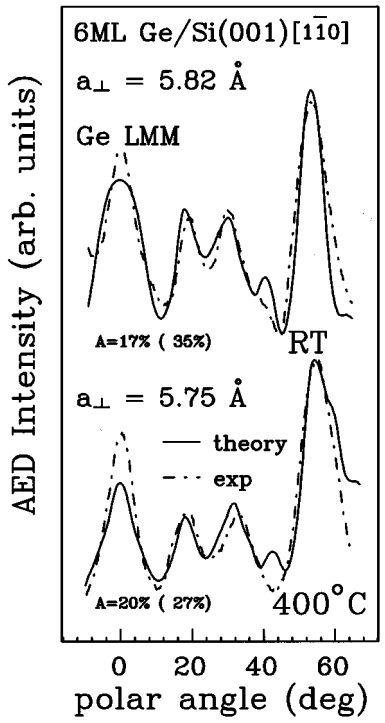

FIG. 8. Best fit of an experiment performed by Diani *et al.* (Ref. 32) at the Ge *LMM* (1146 eV) Auger level on a vicinal surface cut 4° off the [110] direction. Polar patterns are taken along [1$\bar{1}$0] direction. The top experimental curve is relative to deposition of 6 ML of Ge at RT, while the bottom one is 6-ML deposition on the sample kept at 400 °C. In the RT case nine planes of Ge were necessary to fit experimental data. A value of 5.82 ± 0.02 Å for the out-of-plane lattice parameter is obtained, while a value 5.75 ± 0.02 Å was found for the 400 °C experiment. Values of the AED anisotropy for the experimental and theoretical curves are reported.

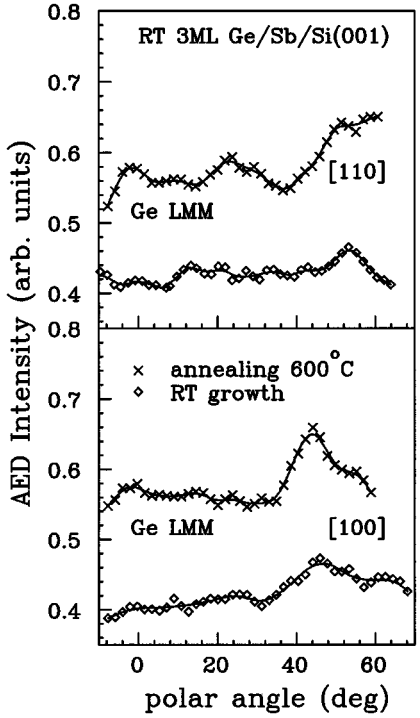

FIG. 9. Polar AED measurements along [110] (top) and [100] directions (bottom) of Ge *LMM* after 3 ML of Ge deposition on 1-ML Sb/Si(001) substrate kept at RT and subsequently annealed at 600 °C.

signal coming from Ge. Furthermore, polar patterns from 3*d* Sb show no diffraction structures in either the cases of deposition on clean Si(100) or with successive deposition of a Ge layer, showing evidence of floating to the surface of the whole Sb layer. In Fig. 9 we report the polar pattern of Ge *LMM* Auger level for 3 ML of Ge deposition on the 2×1-1 ML Sb/Si(001) surface. The measurements performed after deposition at RT are compared with those taken after the annealing of the sample at 600 °C for 15 min. We note the absence of the feature at 0° polar angle emission for RT-deposited Ge layers, while other features are present showing the full crystalline structure of this overlayer. By comparison with the theoretical calculations reported in Figs. 5 and 6, we conclude that this film is continuous, in contrast with the 3-ML Ge deposited at RT (already shown in Fig. 4) where we observed a sizable interdiffusion. Furthermore, after annealing at 600 °C, the appearance of the intensity peak at 0° polar angle emission is a fingerprint of a 5–6-layer contribution to XPD. This conclusion can be obtained on the basis of the theoretical calculation reported in Figs. 5 and 6.

In the case of 6-ML deposition of Ge on 2×1–1-ML Sb-Si(001) surface, we kept the sample at 400 °C during evaporation. In this case the experimental electron-diffraction results are shown in Fig. 10 for the Ge *LMM*

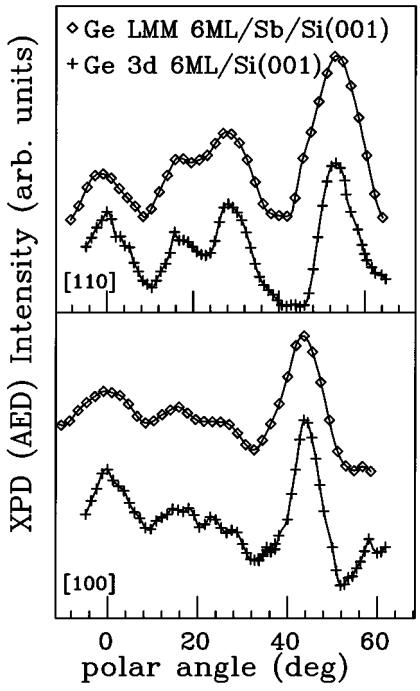

FIG. 10. Experiment with AED Ge *LMM* (1146 eV) on 6-ML Ge/Sb/Si(100) grown at 400 °C compared with experiment done without Sb on the anisotropy of Ge 3*d* (1390 eV). The upper and lower panels refer to [110] and [100] directions, respectively.

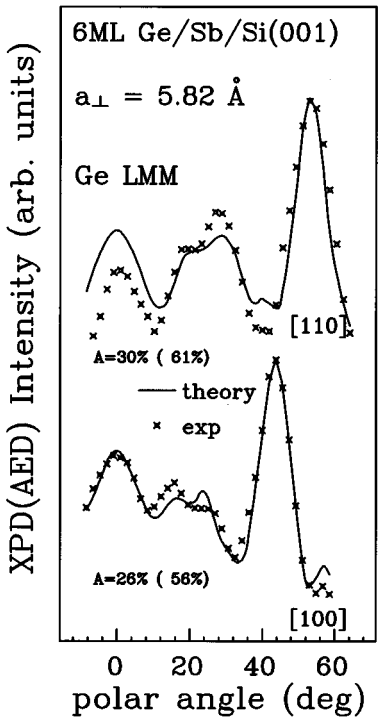

FIG. 11. Best-fit comparison between theory and experiment for the case of XPD of the Ge Auger *LMM* level from 6-ML of Ge deposited on the 1-ML Sb/Si(001) substrate kept at 400 °C. The emission direction is along [110] (top curves) and [100] (bottom curves). A value of 5.82 Å for the out-of-plane lattice parameter in the Ge overlayer was found. The values of the AED anisotropy for experimental and theoretical curves are reported.

Auger line. In this figure the comparisons of the experiment performed with and without surfactant are shown for the polar patterns taken along [110] and [100] directions. In Fig. 11 we report the best fit for 6 ML of Sb-mediated growth of Ge. As can be observed, a great amount of strain (corresponding to a perpendicular lattice parameter $a_\perp = 5.82 \pm 0.02$ Å) is obtained after the fit. The differences from the growth at 400 °C without surfactant are sizable, and far from the error in the angle determination. We also report the monitored RHEED pattern during the growth, as shown in Fig. 12. No hints of relaxation of the in-plane lattice parameter and no island formations were found during the growth with Sb.

VI. DISCUSSION

A. Ge coverage less than limit thickness

Evaluation of the interface quality is a very important task in heteroepitaxial growth. XPD seems to be adequate in pursuing such a task. For example, if we look at Fig. 4 we can easily conclude that Ge/Si(001) at RT grows in a crystalline way, as already pointed out by Diani et al.[26] because of the presence of pronounced features in the diffraction patterns. With a sizable disorder on the surface, these features would be replaced by a smooth background as observed on the 7×7-Si(111) surface,[36] where a large number of adsorption sites introduce a great degree of disorder and the growth of an amorphous layer occurs. A further check of the crystalline

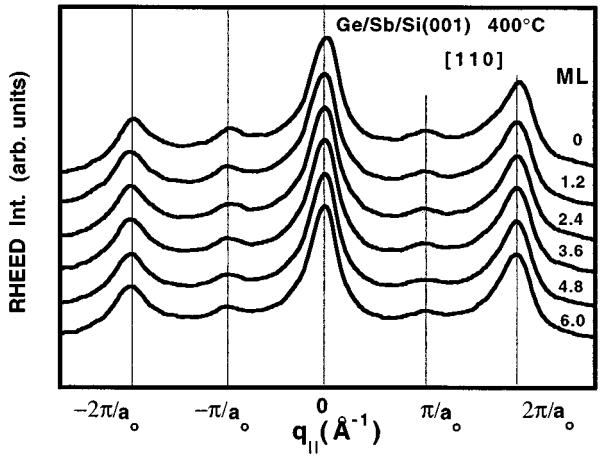

FIG. 12. RHEED pattern during 6-ML Ge deposition on 1-ML Sb/Si(001) at 400 °C. The curves are line scans of the intensity on the phosphor screen taken parallel to the shadow edge and showing the (± 1) and $(\pm \frac{1}{2})$ order of the zeroth-order Laue zone. The electron beam was incident along the [110] direction.

nature of the film is obtained from RHEED, in agreement with a previous work of Miki, Sakamoto, and Sakamoto.[37] In this work the authors also reported the striking observation of a large number of undamped intensity oscillations, testifying to the high quality of the layer-by-layer growth of RT Ge/Si(001). The presence of the XPD peak in normal emission is an evidence of an increase, with respect to the nominal coverage, of the number of layers giving rise to the observed photoelectron diffraction signal. In an analogous experiment Chambers and Loebs[4] reported results from 4 ML of Ge grown at 400 °C almost without evidence of direct normal emission from Ge atoms. In the same paper the case of Si/Ge(001) deposition was studied. When compared with this last experiment, it is almost clear that the intensity of the emission along the normal to the surface is much less in the case of Ge/Si(001). The reason why this effect is small is due to the onset of the intermixing, which is expected to be close to 2–3-ML deposition, while in the Si/Ge(001) case segregation occurs from the early stages of deposition. For the kind of mechanism which is considered to take place, i.e., atomic exchange due to the strain induced by the reconstruction,[38] it is in fact reasonable that the intermixing process could be activated only after a minimum number of layers is achieved. This picture is also coherent with recent total-energy calculations,[39] which have shown, after 2.5 ML of Ge deposition, a significant energy of formation (of about 0.1 eV/atom) of the intermixed phase with respect to the abrupt interface.

Emission along the normal to the surface, before the nominal value of Ge ML's was deposited, was obtained by Diani and co-workers for 3 (Ref. 26) and 3.5 ML (Ref. 32) of Ge deposition at 400 °C. This observation is attributed by the authors to a formation of roughness on the surface. Any presence of sizable roughness is excluded on the basis of measurements which have shown surfaces of Ge grown at 400 °C on Si(001) as extremely flat, with missing dimer reconstructions varying from a 2×12 at 1 ML to a 2×8 at 3-ML Ge deposition.[40] Even less roughness is expected to be present at RT, as also observed on the basis of RHEED intensity oscillation measurements.[37] In addition, the well-

defined and elongated RHEED streaks make us exclude clusters and/or roughness formation.

A very different behavior is observed in the case of Sb-mediated growth when Ge diffusion is inhibited. The growth is layer by layer, with the surface becoming rougher at the increase of the temperature, as already shown in Fig. 9 for the case of the annealed sample at 600 °C. In fact, after the deposition at RT reported in Fig. 9, a marked difference in the XPD features, compared with those ones of Fig. 4, makes us conclude about the absence of any interdiffusion and/or roughness before the annealing. This is an additional prove that the roughness cannot play the role claimed by Diani and co-workers[26,32] during the first stage of Ge deposition. Indeed, a similar effect should be even more evident in the case of 3-ML deposition in the presence of Sb reported in Fig. 9. Horn-von Hoegen and co-workers[40] have shown that the value of the roughness is much higher in the case of Sb predeposition with formation of ''hut'' clusters at very high-temperature deposition. Atoms, in fact, have sufficient energy to reduce strain by occupying ordered positions in the ''hut'' clusters (the kinetic pathways[41]). But before achieving this stage (obtained in the present experiment only after a post-growth annealing at $T \geqslant 600$ °C), the growth is layer by layer, because we did not observe the appearence of the XPD features, characteristic of a Ge-Si compound formation, as we detected in the case of 3-ML growth without Sb.

B. Ge coverage greater than limit thickness

For coverage in excess of the limit thickness, in the presence of a high temperature (400 °C) of the substrate and without surfactant, (Fig. 7 and the lower panel of Fig. 8), we obtained an out-of-plane lattice constant of 5.75 ± 0.02 Å from XPD analysis. This value corresponds to a tetragonal distortion lower than expected for a fully strained film from the elasticity theory. In addition, RHEED patterns showed the appearance of spots (which indicates a transition to a 3D growth) and an expansion of the 2% of the in-plane lattice parameter (Fig. 2). We interpret these experimental results as due to the following growth process: in the presence of a sufficiently high temperature of the substrate, evaporation of dimers rows are possible, as observed by Köhler *et al.*[40] for less than 3-ML deposition, resulting in a partial relaxation of the strain; as the in-plane lattice parameter keeps in relaxing, as we observed by RHEED, it allows the growth of dislocation-free islands with a substantial relaxation of the strain energy. In this way, the growth of coherent islands on a partially strained film occurs. The measurement of the strain for 6 ML is in any case only slightly affected by this continuous relaxation because it involves only the top layer of the surface.

XPD anisotropy during this stage of island formation would result in a steady-state value close to that given by 3–4 ML of the thermodynamically stable continuous layer, as reported by Diani *et al.*[26] An intermixed phase, in the case of the absence of any sizable roughness[40] on the surface, must be invoked in order to justify the discrepancy between the experimental and theoretical anisotropy. As observed from the comparison with theory reported in Fig. 7, instead of the expected 3–4-ML contribution to the anisotropy, in the case of growth in the presence of islands, an experimental anisotropy comparable with a full contribution from six planes of scatterers is obtained. Furthermore, a careful analysis of the width of the diffraction feature along the [101] direction shows that the XPD signal is basically built up by the contribution due to the strained Ge film. Any other contribution induced by unstrained Ge islands (or roughness) would produce a broadening and a possible shift toward the appropriate value relative to an unstrained film. From this analysis we conclude that the contribution of the Ge islands is negligible, and that the six planes we need to fit the experimental data are due to the existence of an intermixed phase.

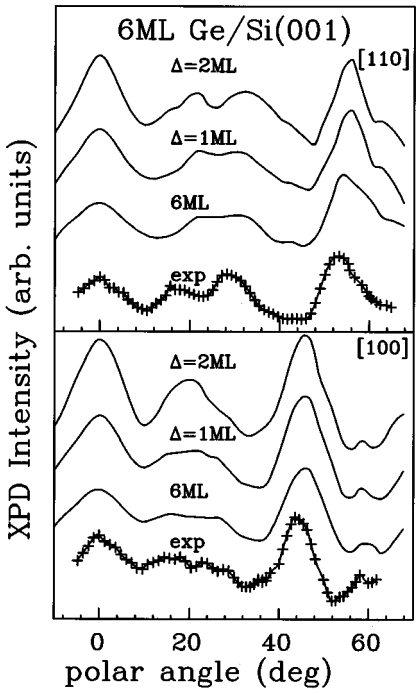

FIG. 13. Comparison with XPD patterns (crossed points) obtained on a 6-ML Ge film deposited at 400 °C on 2×1-Si(001), of theoretical simulation of roughness on the surface. The Ge planes are considered unstrained and unreconstructed. From bottom to top is shown (1) an overlayer without roughness built up by six planes of Ge atoms, the those used in previous comparisons (bottom curve); (2) surface with 1 ML of roughness for a model described in the text (middle curve); and (3) surface with 2 ML of roughness.

Though roughness on the surface grown without Sb was excluded on the basis of LEED with spot profile analysis and scanning tunneling microscopy measurements, showing an extremely flat 2×8 missing dimer reconstructed surface,[40] in this paper we have analyzed the possible effect induced by a sizable roughness. This was evaluated by calculation of clusters of constant number of atoms with arranged square basis islands as in a chessboard. In Fig. 13, from bottom to top, are shown (1) an overlayer without roughness built up by six planes of Ge atoms, (2) a surface with 1 ML of roughness, and (3) a surface with 2 ML of roughness. The roughness is defined as half the value of the amplitude of the surface modulations on the continuous layer. The out-of-plane lattice parameter is kept unstrained, as it is not crucial for this analysis. From this model we can conclude that a roughness contribution, if present, would increase the resemblance of

the XPD pattern with that relative to a thicker layer, resulting in wrong relative intensities of the diffraction features.

About the growth of Ge on Si(001) at RT, our observations are in agreement with results reported in literature of layer-by-layer growth mode without in-plane lattice parameter relaxation.[37] From our fitting of the Diani *et al.*'s experimental XPD curves,[32] we conclude that, in the absence of island formation taking place at the growth temperature of 400 °C and any roughness (the atoms always stick in the most probable position, resulting in a very flat sample), intermixing provides for the 2–3-ML of difference between the nine planes needed to the theory to reproduce the experimental XPD (top panel of Fig. 8) instead of the nominal coverage of 6 ML of Ge. In this case of RT deposition, the lack of strain relaxation (dimer rows evaporation) well explains the higher value of the tetragonal distortion of 5.82 ± 0.02 Å obtained, in good agreement with the value provided by the elasticity theory, when compared with that obtained for the growth at 400 °C

Finally, in the case of Sb predeposition, effects coming from roughness cannot be excluded on the basis of reported SPA-LEED data.[40] In this case Sb results effective in preventing diffusion for (a) the formation of islands, and (b) intermixing. The absence of other channels of relaxation allows, when sufficient thermal energy is available, a kinetic pathway toward the formation of microroughness and ''hut'' clusters.[40] In our investigation neither hints of island formation nor relaxation of the in-plane lattice parameter are observed. Furthermore roughness and intermixing effects can also be excluded until a high-temperature treatment (600 °C) of the sample is operated. This results in a full amount of tetragonal distortion (5.82 ± 0.02 Å), as obtained by our XPD measurements.

VII. CONCLUSIONS

In conclusion we have shown that a careful analysis of the XPD and/or Auger electron diffraction (AED) patterns can provide useful information about the morphology of the Si-Ge interface which goes beyond the straightforward determination of the strain content in the film. In this paper we have singled out different effects coming from intermixing and from roughness at this interface. We have performed the experiment in three different conditions: (1) growth of Ge on Si(001) at room temperature; (2) growth of 3 and 6 ML of Ge on the sample kept at 400 °C, and, finally, (3) growth of Ge in the presence of a surfactant (Sb). We have found evidence of intermixing after deposition without a surfactant at both temperatures of the sample. The behavior at RT points to a layer-by-layer growth, because of the limited kinetics on such a surface. The determination of strain content in the two cases has shown a higher amount of strain for the film grown at RT with respect to that grown at 400 °C, because a freeze of the strain relaxation mechanism takes place at the interface. The presence of a sizable roughness is excluded by a comparison with the experimental behavior in the presence of a surfactant, by theoretical simulation, and on the basis of previous experimental evidence reported in literature. With a surfactant predeposited on the surface the great reduction of the kinetics allows layer-by-layer growth, and prevents any interdiffusion. Only strong annealings at 600 °C lead to a sizable intermixing and/or roughness of the film, as observed in literature. The present results enforce our confidence in the right use of Sb as a surfactant to obtain very sharp Si/Ge interfaces, if post-growth annealings at temperatures greater than 600 °C are avoided. Without Sb a thin region of interdiffusion at the Si/Ge interface has been always observed, thus addressing the problem of the role played by the thin intermixed interfaces in the setup of the interesting optical properties of Si-Ge materials.

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