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Reconstructions upon thermal desorption in ultra high vacuum of InSe covered Si(111) surfaces

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Abstract. At an InSe/Si(111) heterostructure, the transition between the cubic Si substrate and the layered compound InSe remains a problem. The surface structure of InSe films grown by molecular beam epitaxy on Si(111) substrates has been studied under ultra high vacuum by low energy electron diffraction, Auger electron spectroscopy, and helium atom scattering upon sequential thermal erosion of the film until full removal. Between the initial 1 × 1 diagram of InSe(001) and the In-induced $\sqrt{3} \times \sqrt{3}$ R 30° pattern of Si(111), two intermediate stages were observed. One, above the single layer coverage range, corresponds to the coexistence, over a strained bonding half-layer, of InSe layers strained to the Si parameter and of others which are relaxed to bulk InSe parameter. The second stage, below the half-layer coverage range, is characterized by a nearly 5 × 5 mesh of Si(111) which could arise from two-dimensional islands made of both In and Se.

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1 Introduction

The compounds GaSe and InSe are characterized by highly anisotropic properties due to their layered structure where iono-covalent bonds are essentially confined within the layers whereas the interactions between layers are very weak, mainly of van der Waals type. Each primitive layer has hexagonal symmetry and comprises four atomic planes in the sequence Se-M-M-Se where M stands for Ga or In. The formation of heterostructures between these III-VI semiconductors and a covalent cubic semiconductor such as silicon is a challenge because of their potentialities for non-linear optics or as intermediate between highly mismatched semiconductors. In the latter case, it is important to know whether strains exist in the vicinity of the interface.

Such III-VI/Si(111) heterostructures can be prepared by a molecular beam epitaxy (MBE) technique [1]. High resolution transmission electron microscopy (TEM) revealed that the so-formed interfaces are abrupt both in GaSe/Si(111) [2] and InSe/Si(111) [3] systems.

In order to study such systems when a fairly thick film (100-300 Å) has been deposited onto Si(111), a thermal procedure has been used in ultra high vacuum (UHV) to thin down the film and progressively reach the interface. In the course of this treatment, the interface structure can hopefully be revealed. But also, stresses can be relaxed and atoms can migrate eventually leading to new structures.

A previous study using this procedure has been reported for the system InSe/Si(111) in which the substrate was initially a 7 × 7 reconstructed surface [4]. In that study, the interface electronic properties were investigated from the evolution of the photoemission yield spectrum in relation with structural and compositional changes. Here, we focus on the surface structures observed during thermal erosion of such systems as well as of similar systems for which the substrate was initially an unreconstructed chemically hydrogenated Si(111) surface. Structural information have been derived from low-energy electron diffraction (LEED) and from elastic helium atom scattering (HAS). Information on surface composition were obtained from Auger electron spectroscopy (AES).

2 Experimental information

The heterostructures were prepared in the Paris laboratory by a MBE technique. The substrates were wafers 300 μm thick and 2 inches in diameter, from low-doped

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n-type Si, oriented within 0.15° along the (111) face. They were chemically hydrogenated [5] prior to introduction in ultra high vacuum. The Si(111) 1×1 -H substrate was used as such or converted to Si(111) 7×7 by heating at 600 °C in UHV [6]. The InSe film was grown on the substrate held at 450 °C, by co-deposition of In and Se with an equivalent partial pressure ratio $P_{\mathrm{Se}}/P_{\mathrm{In}} \approx 3$.

The formation of the InSe compound was monitored by reflection high-energy electron diffraction (RHEED) during deposition. It revealed the same epitaxial relations as with GaSe/Si(111) [1], namely: InSe(001) // Si(111) and InSe[100] // Si[$1\bar{1}0$]. Samples with appropriate size were cut out of the wafers. They were kept in a desiccator, under primary vacuum, or in dry nitrogen prior to being mounted in the analysis chamber, either in Paris [7] or in Göttingen [8]. Several heterostructures in which the InSe film had a nominal thickness ranging from ~ 150 to ~ 330 Å (*i.e.*, from ~ 18 to ~ 40 primitive layers) have been investigated.

In the Paris laboratory, the thermal treatment of the InSe/Si system was performed through direct Joule heating by rapidly setting the current at a given value and maintaining it for about 5 minutes while the temperature was read with an infrared (IR) pyrometer. The heating current was increased from one annealing to the next so that the highest temperature reached could be in the 700–800 °C range. After each annealing, when the sample had cooled down to room temperature (RT), the system was examined by LEED with a Riber diffractometer, and characterized by AES with a Varian cylindrical mirror analyzer (CMA). For AES, a primary electron beam 2 keV in energy was used, and the Auger lines of Se, In and Si at 41, 399 and 91 eV respectively, were recorded. Altogether, six samples from four different heterostructures were investigated by this approach.

The HAS experiments were carried out in Göttingen with a highly monoenergetic atom beam. The direction of the incoming atoms, of wave vector $\mathbf{k}_i$, and that of the outgoing ones, of wave vector $\mathbf{k}_s$, were at 90.1° from each other. Diffraction peaks were scanned by rotating the sample around a surface axis perpendicular to the scattering plane ($\mathbf{k}_i$, $\mathbf{k}_s$). Thus changes in the wave vector component parallel to the surface were explored along the azimuth coincident with the trace of the scattering plane. The sample could be heated resistively. The two InSe/Si(111) samples that were used in the HAS study were subjected to different thermal treatments. In order to avoid contamination, one sample, from a InSe/Si(111) 1×1 -H heterostructure, was heated to 150 °C prior to bake-out of the chamber; the heating current continued to go through the sample during bake-out at 200 °C for about 24 hours. The actual temperature of the sample during this bake-out was then close to 350 °C. The other sample, from a InSe/Si(111) 7×7 heterostructure, was not directly heated during bake-out which lasted about 12 hours at 150 °C. After the bake-out, an elastic HAS profile was measured at RT. Afterwards, the sample was heated in ultra high vacuum. The temperature, monitored with an IR pyrometer, was increased by steps of about 25 °C, waiting at each step that the permanently measured helium specular intensity became constant. Once in a while the heating was stopped and the diffraction profile was checked at RT. The highest temperature reached in this process was 350 °C for the InSe/Si(111) 1×1 -H sample, and 440 °C for the other one.

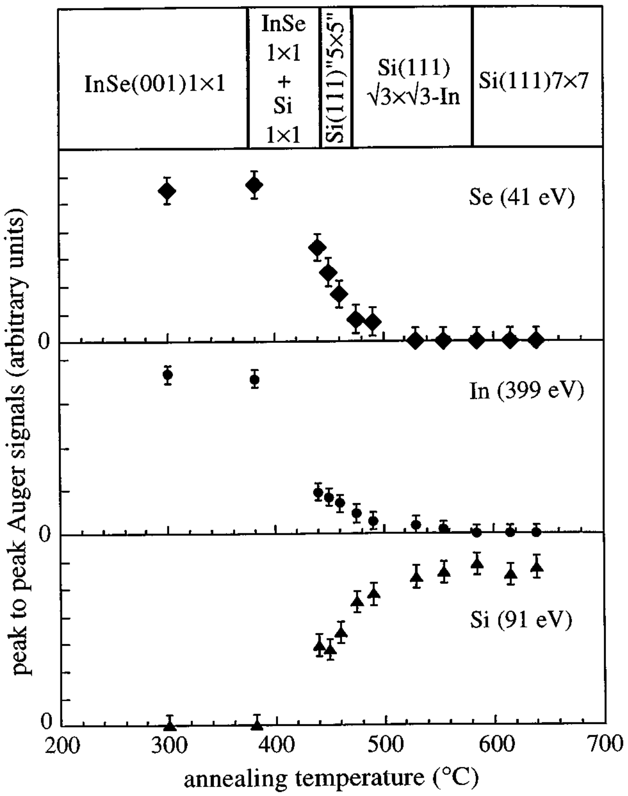

Fig. 1. Evolution of the Auger peak intensities of Se, In and Si as a function of annealing temperature upon thermal erosion in ultra high vacuum of an InSe film, about 175 Å thick, grown on a Si(111) 1×1 -H substrate. The unit meshes observed in LEED are given at the top of the figure.

The thermal procedures were therefore fairly different in the two sets of experiments, and prevent a direct comparison of the effects of a given temperature.

3 Results

Typical LEED and AES results are illustrated in Figure 1. The peak to peak intensities of the Auger lines of Se, In and Si are plotted as a function of annealing temperature T_A for a InSe/Si 1×1 -H system. In the upper part, we give the sequence of surface unit meshes observed in LEED and their temperature ranges. As T_A is raised, various surface structures appear, always in the same order as described below, the same as reported previously for a InSe/Si 7×7 system [4]. This similarity in behaviour upon desorption suggests there is no fundamental difference between the heterostructures formed with InSe on Si(111) substrates having different well-ordered initial structures; this is consistent with what has been observed by TEM

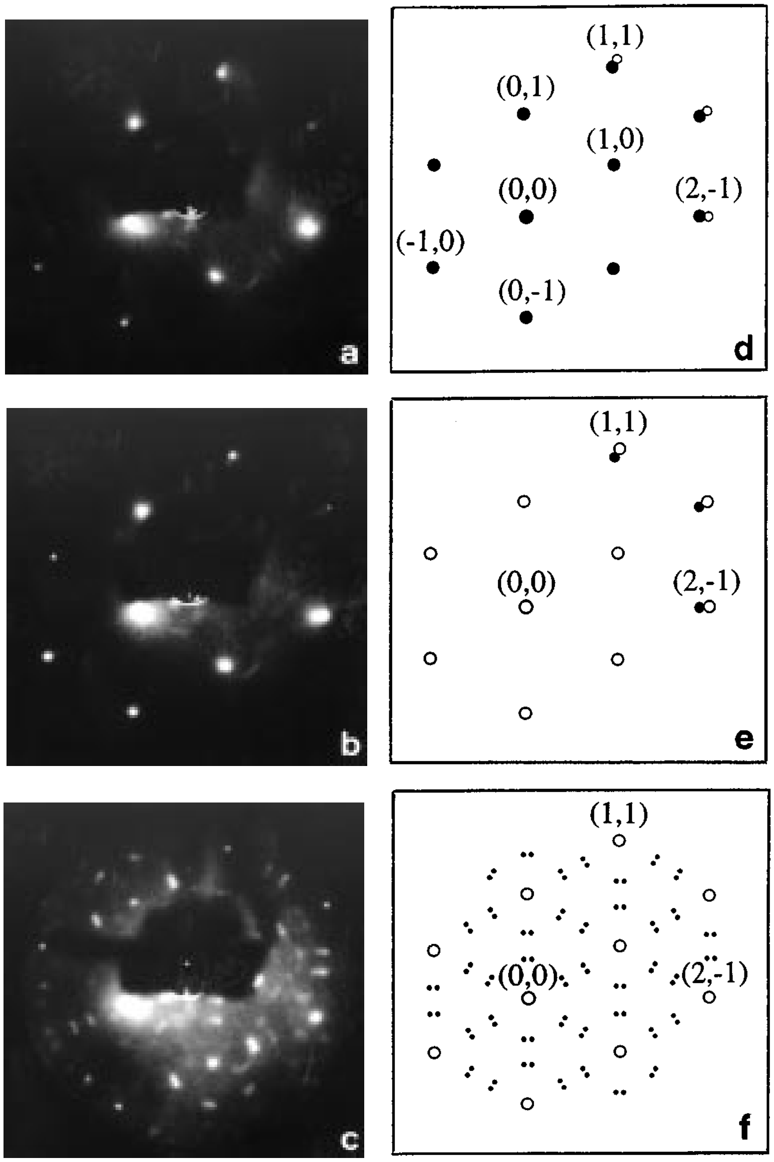

Fig. 2. LEED patterns observed in the course of thermal erosion in ultra high vacuum of a InSe film grown on a Si(111) 1 × 1 -H substrate: (a) $E_p = 64$ eV, $T_A = 380$ °C; (b) $E_p = 64$ eV, $T_A = 440$ °C; (c) $E_p = 60$ eV, $T_A = 450$ °C. Schemes of the LEED patterns: (d) and (e) correspond to (a) and (b) respectively (The dots represent the diffraction beams from InSe(001) and the circles are those from a Si(111) 1 × 1 lattice; where the beams from the two structures are not resolved, the symbol of the dominant structure is used); (f) represents the pattern from the "5 × 5" superstructure (The circles are the integer order diffraction beams; the doublets are the $2/(\sim 5)$ fractional order beams).

on GaSe/Si(111) systems [2]. In spite of the differences in thermal procedure, the HAS results give a sequence of diffraction profiles which correlates very well with the LEED results. The surface structures observed are the following.

Stage (A): At temperatures lower than about 380 °C, the diffraction properties are those of the layered compound. Sharp hexagonal LEED patterns are observed which are consistent with the InSe(001) 1 × 1 surface unit mesh. The diffraction profiles in HAS, as observed with the InSe/Si(111) 7 × 7 sample, show very narrow peaks at positions giving the same lattice parameter as bulk InSe(001). During that stage, the InSe coverage remains thick enough so that the Auger signal intensities of In and Se do not change, and the Si substrate is not observable.

Stage (B): For T_A around 420 °C, new spots appear in the LEED pattern which are well resolved beyond the first order hexagon (Figs. 2a and 2b, and schemes Figs. 2d and 2e). They are farther away from the (00) beam as compared to the InSe spots, at positions indicating a 4% decrease of the surface mesh parameter. They are thus consistent with the Si(111) 1 × 1 mesh (the surface parameters along the investigated surfaces are $a_s(\text{Si}) = 3.84$ Å, and $a(\text{InSe}) = 4.002$ Å [9] to 4.05 Å [10] depending on which polytype is considered). For the particular sample of Figure 1, this occurs from 380 °C up to 440 °C. At 380 °C (Fig. 2a), the InSe diffraction beams are much more intense than the new ones; it is the reverse at 440 °C (Fig. 2b).

A comparable observation is made in elastic HAS when extra peaks, giving the Si(111) parameter, show up in the diffraction profiles. This is illustrated in Figure 3a along the $[11\bar{2}]$ azimuth of the Si substrate for the InSe/Si(111) 1 × 1 -H sample cut out of the same wafer as sample of Figure 1 (the diffraction profile of Fig. 3a has been observed, after bake-out, from RT to 350 °C without any significant changes which is consistent with an actual sample temperature of about 350 °C during bake-out). The peak giving the Si parameter is well resolved from that corresponding to InSe in the second order diffracted beams, whereas only a shoulder shows up at first order. The features associated with InSe parameter are the most intense in Figure 3a. In Figure 3b, we give another example of this situation for the InSe/Si(111) 7 × 7 sample after annealing at $T_A = 420$ °C during 30 minutes. In Figure 3b, conversely to Figure 3a, the features corresponding to the Si parameter are the most intense.

Stage (C): Then, around $T_A = 450$ °C, a new pattern is revealed in LEED (Fig. 2c, and scheme Fig. 2f) which we shall refer to as "5 × 5". It is a pseudo 5 × 5 structure of Si(111) slightly misoriented by $5° \pm 0.5°$ with respect to the primitive cell of the substrate and where equivalent domains have formed. The pattern is characterized by fairly intense doublets of order $2/(\sim 5)$ forming an hexagon around each integer order beam of Si(111). These fractional order hexagons have roughly the same orientation as the first order one from Si. Depending on the sample, the doublets are not always resolved as in Figure 2c but may appear as single elongated spots, especially when InSe had been deposited on Si(111) 7 × 7. This appears consistent with a better quality of the initial heterostructure when it is formed on a smooth substrate like Si(111) 1 × 1 -H, similarly to what has been observed with GaSe/Si(111) [2].

This situation can be correlated to a diffraction profile from HAS in which new diffraction peaks are observed along the investigated azimuth (Fig. 3c) after the InSe/Si(111) 7 × 7 sample had been annealed at 440 °C for 15 minutes. The extra peaks give, for the ratio of the real space lattice parameter as compared to that of Si(111), an average value of 5.3 ± 0.1 (*i.e.*, with an accuracy of 2% which is not attainable with the LEED diagram pictures). Their full width at half maximum is about twice that of the substrate peaks.

Stage (D): At higher temperatures (roughly in the 500 °C range), a Si(111) $\sqrt{3} \times \sqrt{3}$ R 30° pattern is observed. It is most intense when Se is no longer detectable in AES and only In is left on the substrate. At that stage, the Auger results from the In-induced reconstruction are consistent with AES measurements performed during the deposition of In onto Si(111) [11] and indicate that the In coverage is about 1/3 of a monolayer (1 monolayer on Si(111) corresponds to 7.8×10^{14} atoms/cm^2). Finally, at still higher temperatures ($T_A \geq 580$ °C), the clean substrate, 7 × 7 reconstructed, is recovered, sometimes after an intermediate 1 × 1 pattern.

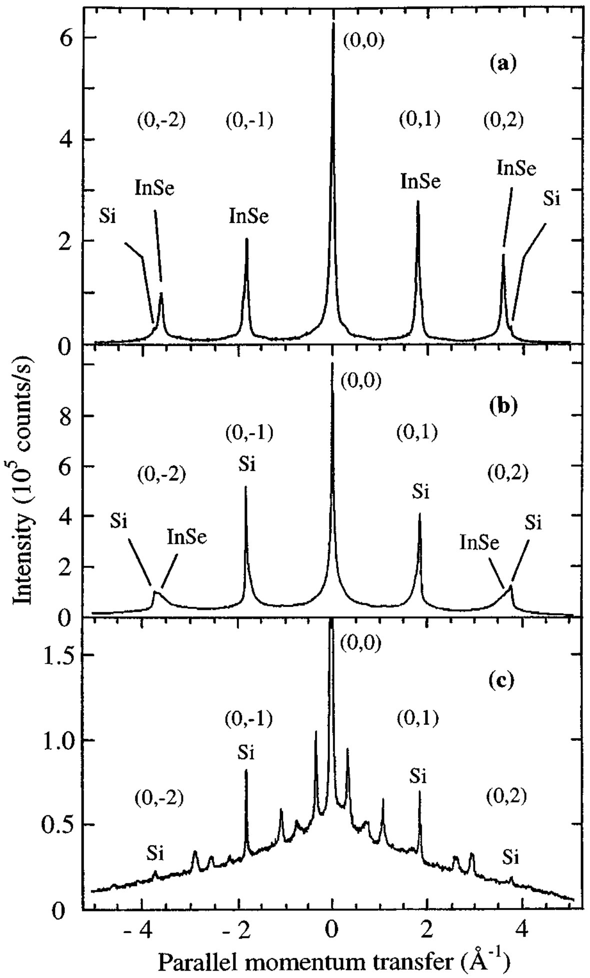

Fig. 3. HAS diffraction profiles measured in the course of thermal erosion in ultra high vacuum of InSe films grown on a Si(111) 1 × 1 -H substrate (a): $T_A \approx 350$ °C; or on a Si(111) 7 × 7 substrate (b): T_A= 420 °C, and (c): $T_A = 450$ °C. The helium atoms had a wavevector $k_i = 6.2$ Å^{-1}. The parallel momentum transfer is along the $[11\bar{2}]$ azimuth of the substrate.

Information on the thickness of the InSe film left on the substrate during stages (B) and (C) have been derived from the AES measurements. For that purpose, we have used the macroscopic model of a flat and abrupt interface between the Si substrate and a film of uniform thickness d at all stages. The intensity of the Auger peaks depends then on d as well as on the Auger electron escape depth λ taken equal to 5, 12 and 6 Å for Se, In and Si respectively [12]; these values take into account the atomic density of the material which the electrons go through, and the emergence angle of the electrons detected at the CMA. In the case of Se (as well as In), the intensity I has been compared to its value I_∞ measured during stage (A) when the film is very thick, so that $d = -\lambda \ln(1 - I/I_\infty)$. In the case of Si, the intensity I has been compared to its saturation value I_0 measured during stage (D) when the InSe film has completely desorbed, so that $d = -\lambda \ln(I/I_0)$. Taking into account all the investigated samples and annealing temperatures, the film thickness ranges from 19 Å or more (when Si is not detectable) to ~ 4.3 Å in the case of stage (B), and from ~ 10 Å to ~ 1.5 Å in the case of stage (C). For each element, a mean film thickness $\langle d \rangle$ has been determined from the value of I/I_∞, or I/I_0, averaged over all the experimental values that apply to a given stage. The results agree within 10% dispersion and give $\langle d \rangle = 11.6$ Å for stage (B), and $\langle d \rangle = 3.6$ Å for stage (C). The good agreement between the $\langle d \rangle$ values obtained from In and Se in particular indicates that, on average, the In/Se atomic ratio does not change significantly up to stage (C) included.

4 Discussion

The discussion will concern stages (B) and (C) which are characteristic of the InSe/Si(111) system when both In and Se are still present on the substrate but at such coverages that the interface is close or has been reached. We shall assume that the InSe/Si(111) interface remains abrupt during thermal desorption of the grown film.

4.1 Stage (B): InSe(001) 1×1 + Si(111)1×1

At this stage, in LEED and elastic HAS as well, diffraction features associated with the lattice parameter of both InSe(001) 1×1 and Si(111) 1×1 are observed simultaneously while the substrate is still covered up by In and Se. A similar observation has been made by elastic HAS [13], but not by LEED [14,15], on GaSe/Si(111) heterostructures to which the same thermal approach had been applied. The formation of interfacial dislocation gratings has been considered, much like in the Ge/Si(111) system [16]. However, the LEED pattern we get here (Figs. 2a and 2b) is quite different from what is observed in that case where each normal order spot would be split into a regular hexagonal array of satellites [16]. Our observations, both in LEED and elastic HAS, are consistent with the presence of two types of regions on the surface, some having the unit mesh of InSe(001) 1×1, while others have the surface unit mesh of Si(111) 1×1. The latter extend in area as the annealing temperature is raised.

We do not think that the regions having the surface unit mesh of Si(111) 1×1 correspond to the substrate itself. (i) This structure has been observed (Fig. 2a) when Si is not detected in AES (Fig. 1, 380 °C). (ii) When this structure is dominant in LEED (Fig. 2b) and Si is detected in AES (Fig. 1, 440 °C), the diffracted beams are so bright and the background is so low that the observed pattern is not compatible with diffraction from the bulk of the Si substrate seen through a disordered film. (iii) If bare silicon were to exist, it would exhibit either a $\sqrt{3} \times \sqrt{3}$ reconstruction because of the presence of In in the system, or a 7×7 reconstruction if it were clean. These reconstructions are indeed observed but at a much later stage of thermal desorption, not at stage (B).

Domains with the surface unit mesh of Si(111) 1×1 have been attributed by El Monkad *et al.* [4] to half a single layer of InSe where a monolayer of In on top of the Si(111) outer plane would be covered by the corresponding monolayer of Se. Whereas, the first full (thickness-wise) layer of InSe would have the InSe parameter, *i.e.*, it would be relaxed. These authors [4] could not ascertain whether the strained half-layer of InSe was present below the grown InSe film. In fact, we expect the strained half-layer of InSe, directly bonded to Si, to have formed during growth by analogy with the GaSe/Si(111) system. In the latter case, such a model of growth has been proposed from a TEM structural analysis [2] performed on 80–400 Å thick GaSe films grown on various Si(111) substrates. This very first stage of growth was confirmed by X-ray standing wave measurements [17] carried out on as-grown very thin GaSe films (with a nominal thickness of ~ 4 Å). The existence of a strained bonding half-layer for InSe/Si(111) as well is consistent with the thickness range lower limit of ~ 4.3 Å as determined from AES, knowing that the c parameter of a primitive InSe layer, perpendicular to its surface, is ~ 8.32 Å [9]. This half-layer, strongly bonded to the Si substrate by In–Si covalent bonds, would be gradually uncovered during the thermal desorption of InSe.

Diffraction beams from domains having the lattice parameter of the substrate can be observed when Si is not detected yet in AES (Fig. 2a; Fig. 1, 380 °C), *i.e.*, when Si is still covered up by an InSe film at least 28 Å thick on average assuming a Si detection limit of 1% I_0. It seems unrealistic to get this result from a system where 1% of the surface explored would correspond to holes “drilled” by the thermal treatment down to the bonding half-layer, through at least three full (thickness-wise) and relaxed InSe layers. For this reason, we think that InSe layers, above the bonding half-layer, might probably also be strained to the substrate lattice. It is consistent with the mean thickness value of 11.6 Å which, not only is larger than half a layer thickness, but is also larger than one layer thickness. Such a possibility seems to occur in GaSe/Si(111) as well [14,15] from LEED and AES results of a thermal desorption study. For the latter system, the presence of strained GaSe layers next to relaxed ones was required in the analysis of grazing incidence X-ray diffraction measurements performed on (unannealed) GaSe/Si(111) [18]. Furthermore, the existence of strained GaSe layers together with the strained bonding half-layer is consistent with the results of a core level study of (annealed) GaSe/Si(111) [19].

Thus during stage (B), the sample surface is approaching the interface down to the strained half-layer of InSe which is directly bonded to Si *via* the In atoms. In the course of this process, it appears likely that strained InSe layers are uncovered and coexist with relaxed ones.

4.2 Stage (C): Si(111)“5×5”

Stage (C) is characterized by the Si(111)“5×5” LEED pattern of Figure 2c and the elastic HAS profile

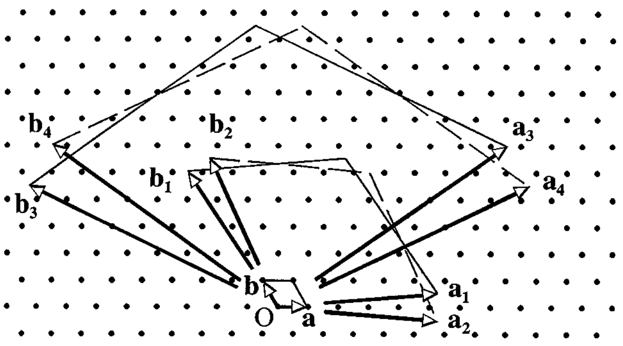

Fig. 4. Real space lattice of Si(111) 1 × 1 defined by $(\mathbf{a}, \mathbf{b})$ showing the unit meshes $(\mathbf{a_1}, \mathbf{b_1})$ and $(\mathbf{a_2}, \mathbf{b_2})$ of Si(111) "5 × 5" and those $(\mathbf{a_3}, \mathbf{b_3})$ and $(\mathbf{a_4}, \mathbf{b_4})$ of Si(111) "$5\sqrt{3} \times 5\sqrt{3}$".

of Figure 3c from a Si(111) 5.3 × 5.3 structure. An In-induced 5 × 5 superstructure has been reported from RHEED during the deposition of In onto Si(111) $\sqrt{3}\times\sqrt{3}$-In [20]. This structure, observed at coverages of 1.0-1.5 monolayer, is not well established though, and the authors assert that it may correspond to the LEED diagram with pseudo-twelve-fold symmetry observed by Lander and Morrison [21]. It is certain that this diagram is quite different from the LEED pattern of Figure 2c. Another In-induced superstructure, Si(111) $\sqrt{31}$-In, has been identified by RHEED during deposition of In onto Si(111) 7 × 7 at various temperatures [22]. This structure has been observed for coverages between ~ 0.45 and ~ 0.8 monolayer, and from ~ 420 °C up to ~ 550 °C. It is not specified whether it is observable at room temperature after cooling down. However, (i) the lattice parameter ratio of $\sqrt{31} = 5.57$ is different, beyond uncertainties, from that of 5.3 determined here by HAS, and (ii) the angle of nearly 9° by which this superstructure mesh is rotated with respect to the Si substrate mesh is much larger than what we observe here. Besides, at stage (C), both In and Se are still present on the surface in similar proportion as in InSe. Thus, the observed "5 × 5" diffraction pattern appears specific of the InSe/Si(111) system rather than of a merely In-induced superstructure of Si(111).

From the information contained in the diffraction features of Figures 2c and 3c, it is possible to propose a unit mesh for the "5 × 5" structure. We shall refer it to the surface unit mesh of Si(111) 1 × 1 defined by vectors **a** and **b** at 120° from each other (Fig. 4), with $a = b = a_s$ (Si). The "5 × 5" structure comprises equivalent domains, because of the symmetry of the substrate, given by the following sets of vectors (Fig. 4):

$$\mathbf{a}_1 = 5.5\mathbf{a} + 0.5\mathbf{b}$$

$$\mathbf{b}_1 = -0.5\mathbf{a} + 5\mathbf{b}$$

and

$$\mathbf{a}_2 = 5\mathbf{a} - 0.5\mathbf{b}$$

$$\mathbf{b}_2 = 0.5\mathbf{a} + 5.5\mathbf{b}.$$

With the usual surface notations, the superstructure is Si(111) 5.27 × 5.27 R (± 4.71°). It accounts for both LEED and HAS results within the experimental uncertainties.

A close examination of the "5 × 5" LEED pattern (Fig. 2c) reveals the presence of faint and wide spots, closer to the integer order spots than the characteristic doublets mentioned previously. Their angular position and distance from the integer order spots are consistent with a "$5\sqrt{3}\times5\sqrt{3}$" structure, more precisely with Si(111) $5.27\sqrt{3} \times 5.27\sqrt{3}$ R (30° ± 4.71°) domains which can be described by (Fig. 4):

$$\mathbf{a}_3 = 10.5\mathbf{a} + 6\mathbf{b}$$

$$\mathbf{b}_3 = -\ 6\mathbf{a} + 4.5\mathbf{b}$$

and

$$\mathbf{a}_4 = 10.5\mathbf{a} + 4.5\mathbf{b}$$

$$\mathbf{b}_4 = -\ 4.5\mathbf{a} + 6\mathbf{b}.$$

What is remarkable about these structures is that: 5.27 a_s(Si) = 5 a(InSe), where a(InSe) is the parameter of bulk InSe. The factor of 5 is obtained with at most 1% deviation depending on which InSe polytype is considered. It suggests that, along the surface, the "Se-In" entities which are at the origin of the "5 × 5" superstructure may have the same parameter as bulk InSe. They are oriented in such a way around the surface normal that registry with the substrate is possible. The initial epitaxial relationship of a thick InSe film is lost at this stage. The large width of the fractional-order features in elastic HAS as compared with that of the integer-order peaks indicates that the "Se-In" entities very likely form islands, isolated from each other, over the sample surface. The lateral extent of these islands should be around 70 Å as estimated from the average value (0.09 Å^{-1}) of the full width at half maximum of the fractional-order peaks in elastic HAS. (One should note that a domain size of about 400 Å has been determined by electron microscopy on (unannealed) InSe/Si(111) samples similar to ours [3]).

One-layer high islands of relaxed InSe over the strained bonding half-layer have been considered for "Se-In", assuming that, locally, the film thickness does not change continuously but by increments of one layer height. This model seems incompatible (i) with the AES results which tell us that the mean film thickness during stage (C) is ~ 3.6 Å, *i.e.*, slightly smaller than half a layer thickness, and (ii) with the fact that the "5 × 5" superstructure has been observed in LEED down to a film thickness of about 1.5 Å over Si. But, above all, registry between "Se-In" and the substrate somehow implies a few fairly strong bonds of covalent nature to anchor one lattice over the other. Although the interactions are not purely of van der Waals type, such strong bonds are unlikely to exist between the Se sheet of a relaxed InSe island and the Se sheet of the strained bonding half-layer which would be the substrate in the model considered.

The Auger results appear more consistent with "Se-In" islands about half a layer thick over Si. In that case, using a very simplified model, the thickness range upper limit of stage (C), ~ 10 Å, would correspond to about 35% of the surface being covered by the "Se-In" islands, and the remaining 65% by 1.5 InSe layer. While at the thickness range lower limit, ~ 1.5 Å, 40% of the surface would be covered by "Se-In". The observed "5 × 5" structure implies that, in such InSe half-layer patches, the constraint previously imposed by the substrate would be relieved. However, relaxed InSe half-layer islands seem unlikely. From our knowledge of other semiconductor/semiconductor systems, any double atomic layer of a semiconductor, bound to a substrate having a few percent mismatch with it, binds epitaxially to it by being properly strained. The best known examples of this are Ge over Si(111) [23] and InAs over GaAs(100) [24] systems, where the deposited layer has a lattice parameter larger than that of the substrate like in the present system.

The unit mesh of the "5 × 5" structure of the InSe/Si(111) system is intermediate between Si(111) 5 × 5 (or rather, in the present context, the 5 × 5 mesh built on the strained InSe bonding half-layer) and Si(111) $\sqrt{31}$-In [22]. As far as the In coverage is concerned, we would expect "Se-In" to be also intermediate between these two extreme situations, *i.e.*, the In coverage would be between 1 and 0.8–0.45 monolayer. In atoms would be bonded to Si forming the necessary strong bonds to have registry with the substrate. Various sites would be involved, among which, very likely, the ternary T_4 site implied in the next stage $\sqrt{3} \times \sqrt{3}$ reconstruction. During annealing, the In-induced $\sqrt{31}$ reconstruction may not be reached because of the presence of Se. AES results point to an atomic composition close to that of InSe. Indeed, there should be enough Se atoms forming bonds with In to impose, parallel to the surface, atomic distances related to those in bulk InSe.

It is interesting to consider the compound In_4Se_3 which has a slight deficit in Se as compared to InSe, a situation which is likely to be encountered at the present stage of annealing of InSe/Si(111) system. It is not possible to relate the "5 × 5" structure we observe to the orthorhombic structure of this material [25] even though the c parameter of In_4Se_3 (4.08 Å) is close to the a parameter of InSe and corresponds to the distance between Se atoms in that direction. However, examination of the In_4Se_3 structure reveals that each Se atom is bound to three In atoms, whereas In is bound either to three Se and one In, or to two Se and two In, or even to just one Se. Thus, there appears a certain stability of the Se bonding as opposed to the variability of the In bonding which very likely come into play in the formation of the "5 × 5" structure of InSe/Si(111).

No stage equivalent to (C) has been observed upon annealing of GaSe/Si(111) systems which, around 630 °C, switch directly from stage (B) to Si(111) $\sqrt{3} \times \sqrt{3}$ R 30° – Ga [14,15]. This difference can be compared to the great ability of In, when deposited onto Si(111), to induce many different reconstructions, which depend on coverage and thermal history of the sample [20–22], whereas only the $\sqrt{3} \times \sqrt{3}$ superstructure is observed when Ga is deposited onto Si(111) [26]. It may be related to the difference in covalent radius between In (1.44 Å) and Ga (1.26 Å) [27].

It should also be noted that the "5 × 5" superstructure has not been observed during growth. It may have been overlooked since it would occur during the very first few seconds of deposition. However, the sample temperature and the partial pressures conditions are so different between deposition and thermal desorption that this reconstruction may not be a stage of the growing process.

Thus, during stage (C), large parts of the Si substrate are covered solely by two-dimensional "Se-In" islands which are about half a InSe-layer thick. In these regions, when, upon thermal erosion, the half-layer does not completely cover the substrate, some of the In atoms are no longer in top bonding positions. A new structure appears rotated by about 5° from the epitaxial orientation of InSe; it is a Si(111)"5 × 5" structure in registry with the substrate, which also bears a relation with the In–Se bonds of bulk InSe.

5 Conclusion

By progressive thermal erosion of InSe/Si(111) heterostructures in ultra high vacuum, it has been possible to get structural information at the interface from the evolution of the diffraction properties. The results are consistent with a bonding of the Si substrate to half a layer of InSe, *via* the cation atoms, like in GaSe/Si(111) heterostructures; van der Waals growth of InSe layers occurs afterwards. This bonding half-layer is strained to the substrate parameter and carries the epitaxial relationship of the thick InSe film. Parts of the first InSe layer(s) over it may be strained as well, the other parts being relaxed to bulk InSe parameter. When the bonding half-layer does not completely cover the substrate, "Se-In" islands are formed in which the InSe epitaxial relation is lost. Some of the In atoms switch from top bonding positions to other ones inducing a Si(111) "5 × 5" structure, rotated by about 5° from the reference mesh.

References

1. V. Le Thanh, M. Eddrief, C. Sébenne, A. Sacuto, M. Balkanski, J. Crystal Growth **135**, 1 (1994).
2. A. Koëbel, Y. Zheng, J.F. Pétroff, M. Eddrief, V. Le Thanh, C. Sébenne, J. Crystal Growth **154**, 269 (1995).
3. A. Koëbel, Ph.D. thesis, University Paris VII, 1997.
4. S. El Monkad, M. Eddrief, J.P. Lacharme, K. Amimer, C.A. Sébenne, Surf. Sci. **352-354**, 833 (1996).
5. G.S. Higashi, Y.J. Chabal, G.W. Trucks, K. Raghavachari, Appl. Phys. Lett. **56**, 656 (1990).
6. V. Le Thanh, M. Eddrief, C.A. Sébenne, P. Dumas, A. Taleb-Ibrahimi, R. Gunther, Y.J. Chabal, J. Derrien, Appl. Phys. Lett. **64**, 3308 (1994).
7. D. Bolmont, P. Chen, C.A. Sébenne, F. Proix, Phys. Rev. B **24**, 4552 (1981).
8. J.P. Toennies, R. Vollmer, Phys. Rev. B **44**, 9833 (1991).
9. J. Rigoult, A. Rimsky, A. Kuhn, Acta Cryst. B **36**, 916 (1980).

10. A. Likforman, D. Carré, J. Etienne, B. Bachet, Acta Cryst. B **31**, 1252 (1975).
11. D. Bolmont, P. Chen, C.A. Sébenne, F. Proix, Surf. Sci. **137**, 280 (1984).
12. M.P. Seah, W.A. Dench, Surf. Interf. Anal. **1**, 2 (1979).
13. J.P. Toennies, A. Glebov, V. Panella, private communication.
14. H. Reqqass, J.P. Lacharme, C. Sébenne, M. Eddrief, V. Le Thanh, Surf. Sci. **331-333**, 464 (1995).
15. H. Reqqass, J.P. Lacharme, M. Eddrief, C.A. Sébenne, V. Le Thanh, Y.L. Zheng, J.F. Pétroff, Appl. Surf. Sci. **104/105**, 557 (1996).
16. M. Horn-von Hoegen, M. Henzler, Phys. Stat. Sol. (a) **146**, 337 (1994).
17. Y. Zheng, A. Koëbel, J.F. Pétroff, J.C. Boulliard, B. Capelle, M. Eddrief, J. Crystal Growth **162**, 135 (1996).
18. N. Jedrecy, R. Pinchaux, M. Eddrief, Phys. Rev. B **56**, 9583 (1997).
19. A. Amokrane, C.A. Sébenne, A. Cricenti, C. Ottaviani, F. Proix, M. Eddrief, Appl. Surf. Sci. **123/124**, 619 (1998).
20. S. Baba, J.M. Zhou, A. Kinbara, Jpn J. Appl. Phys. **19**, L571 (1980).
21. J.J. Lander, L. Morrison, J. Appl. Phys. **36**, 1706 (1965).
22. M. Kawaji, S. Baba, A. Kinbara, Appl. Phys. Lett. **34**, 748 (1979).
23. T. Narusawa, W.M. Gibson, Phys. Rev. Lett. **47**, 1459 (1981); J. Vac. Sci. Technol. **20**, 709 (1982).
24. F. Houzay, C. Guille, J.M. Moison, P. Hénoc, F. Barthe, J. Crystal Growth **81**, 67 (1987).
25. J.H.C. Hogg, H.H. Sutherland, D.J. Williams, Acta Cryst. B **29**, 1590 (1973).
26. *Properties of silicon*, EMIS Datareviews Series No. 4 (INSPEC, 1988), p.754.
27. L. Pauling, *The nature of the chemical bond*, 2nd ed. (Cornell Univ. Press, 1940), p. 179.