Temperature effects in the bonding and growth mode of In on GaAs(110)

R Cimino†, H Öfner‡ and F P Netzer‡

† Laboratori Nazionali di Frascati dell' INFN, Post Box 13, I-00044 Frascati, Italy
‡ Institut für Experimentalphysik, Karl-Franzens Universität Graz, A-8010 Graz, Austria

Abstract. Electron energy loss spectroscopy and high-resolution core level photoemission spectra of the interface formed between In and the GaAs(110) surface at different substrate temperatures and in the transition from low (LT) to room temperature (RT) are presented. We demonstrate that the interface formed after RT In deposition is morphologically different to the one obtained by depositing the same amount of In at LT and subsequently warming up to RT: for RT deposition the In clusters are separated by the bare, unperturbed GaAs surface, whereas on the temperature-cycled surface after the LT → RT transition a monolayer of In bonded to surface As atoms covers the intercluster region. We analyse the bonding of In on the In–GaAs interfaces and discuss the role played by the substrate geometry in determining the kinetics of the system. A mechanism for the observed non-equilibrium effects in the growth mode of In on GaAs(110) is proposed.

1. Introduction

The study of the growth mode of metallic overlayers on clean semiconductor surfaces has attracted much interest in the past decade [1–3]. Major efforts have been devoted to the understanding of the role played by the overlayer morphology to determine the electronic properties of metal–semiconductor interfaces. These studies are important for a fundamental comprehension of the structure of such interfaces as well as for their technological interest. Different modes of metal overlayer growth have been observed [4], the type of growth being determined by the energetically favourable atomic arrangement and by the kinetics of the process which governs the adatom diffusion on the surface. In this respect, the substrate temperature enters as a major parameter since it can drastically affect the surface diffusion. At sufficiently low temperature the adatoms can be frozen in and can only move a few lattice distances. This will result in a 'Poissonian-like' distribution, where the overlayer atoms sit where they reach the surface in a quasi-laminar fashion [4]. A frequently studied example is the indium-on-GaAs(110) system, which is chemically inert at room temperature (RT) or below [5, 6]. On this interface In forms clusters at RT on an otherwise unperturbed surface, while at around liquid nitrogen temperature (LT) the growth is more laminar and In completely wets the GaAs(110) surface [7–12]. Since the change in the growth morphology seems to depend only on the reduced adatom diffusion at LT and not on surface chemistry, one may expect that once the temperature is raised from LT to RT the quasi-laminar indium will diffuse again on the surface, causing the formation of In clusters. This is indeed the case [11], and we address in this paper the detailed analysis of this process. We identify important differences between the interface grown at RT and the one obtained by warming

up the LT-grown system: a wetting In monolayer remains on the GaAs substrate surface in the latter case, on which clustering occurs. This indicates that non-equilibrium and kinetic effects can affect the growth mode of a metallic overlayer in an irreversible way, and we discuss a possible mechanism for such behaviour in the In–GaAs system.

2. Experimental details

The experiments have employed electron energy loss spectroscopy (EELS) in reflection geometry and high-resolution core level photoemission with use of synchrotron radiation. Electron energy loss spectroscopy was performed in an ultrahigh-vacuum (UHV) system (base pressure $< 1 \times 10^{-10}$ mbar) equipped with a concentric hemispherical electron energy analyser (Leybold EA10), which has been used in differential d^2N/dE^2 mode. The total EELS resolution as determined from the width of the elastically reflected primary peak was about 0.6 eV. Ga 3d, As 3d and In 4d core level photoemission lines were measured at both Wiggler/Undulator (U1) end stations at the BESSY storage ring in Berlin, which are equipped with two toroidal grating monochromators (TGM5, TGM6). The overall resolution in the photoemission experiments was about 0.1 eV. Indium was evaporated from a tungsten crucible onto room temperature (RT) or cooled (LT = 100 K) sample surfaces, and the deposition rate was measured by a quartz microbalance. Clean, well ordered GaAs(110) surfaces were prepared by cleaving *in situ* prenotched bars of differently doped GaAs. Only 'mirror-like' cleaved surfaces were used for the experiment in order to avoid the study of surfaces with a high number of defects. Coverages are given in ångstroms: one monolayer (ML) of In (as referred to the same number of In atoms as atoms on the GaAs(110) surface) is equivalent to 2.4 Å.

3. Results and discussion

To give an overall impression of the different temperature dependent growth modes of indium on the GaAs(110) surface we investigate first the EELS spectra shown in figure 1. The left-hand panel shows EELS of the In–GaAs(110) interface grown at RT, while the right-hand panel shows the spectra collected from the same interface grown at LT. The clean GaAs(110) surface is characterized by (as labelled in the bottom spectrum of figure 1, left panel) (a) two valence band to conduction band transitions at around −3.7 and −6 eV loss energy, (b) the surface plasmon at −10.4 eV, (c) the bulk plasmon at −16.2 eV, (d) the Ga 3d surface exciton at −20.2 eV, and (e) the transitions between the Ga 3d and conduction band states at −21 eV loss energies [7]. The Ga surface exciton (d) involves excitation from the Ga 3d level to the empty dangling bond surface state on the Ga atom, and is thus particularly sensitive to changes in the electronic environment of Ga surface atoms. After In deposition at the surface three additional structures are observed (as labelled in the top spectrum of figure 1, left panel): (f) the In surface plasmon at −8.5 eV loss energy, (g) the In bulk plasmon at −11.5 eV, and (h) a broad feature due to transitions between the In 4d and the conduction band at around −17.3 eV.

The striking features observed when depositing In at RT are the appearance of the In metal structures (the surface and bulk plasmons) as early as after only 1–2 Å In deposited (i.e. less than one complete monolayer) together with the persistence of the clean GaAs(110) surface related Ga 3d surface exciton (d) at coverages as high as 8 Å. Such features are a clear indication that In forms metallic clusters on GaAs(110) surfaces, leaving surface regions in between which are clean and unperturbed by In deposition at RT. This is in good agreement with previous observations of Bonapace *et al* [7].
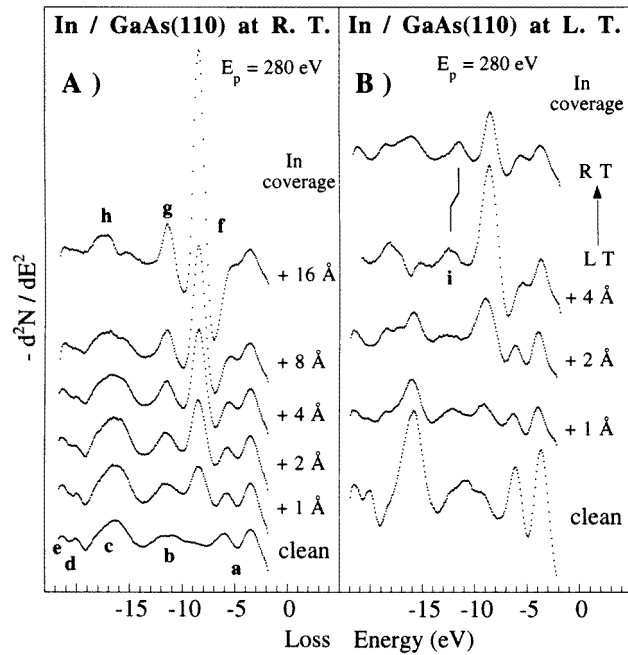
Figure 1. EELS spectra in d^2N/dE^2 form of In deposited onto clean GaAs(110) as a function of nominal In coverage. (A) RT deposition; (B) LT deposition and (top spectrum) warmed up to RT. Electron primary energy $E_p = 280$ eV, approximately specular reflection geometry. The labels on the figure are discussed in the text.

The LT experiments (right-hand panel of figure 1) present a quite different behaviour: the Ga 3d surface exciton disappears after about one monolayer of In coverage and an additional structure grows at -12.4 eV, labelled (i) in the top but one spectrum, which we identify as an interface plasmon. The presence of the interface plasmon (i) indicates that the 4 Å In film is quasi-laminar and does not yet have the bulk properties of a thick In metal film. This, together with the absence of the In bulk plasmon, suggests that the formation of metallic In clusters is strongly inhibited at LT and that In wets the GaAs(110) surface.

The interface formed by depositing 4 Å In at LT and then warming the system up to RT is shown in EELS at the top of figure 1, right-hand panel. Figure 2 displays in more detail the Ga 3d exciton region for the interface formed by depositing 4 Å In onto GaAs(110) at LT, for the interface obtained after warming up to RT, and for 4 Å In grown directly at RT. We note that the In atoms deposited at LT become mobile on warming up and tend to form clusters, as evidenced by the peak shift in the plasmon region, indicating the reduction of the interface plasmon and the emergence of the In bulk plasmon (see the top of figure 1). The most interesting aspect of this surface is that no 'clean' surface is recreated in this process, as shown by the absence of the Ga 3d surface exciton at -20.2 eV in the warmed-up spectrum (figure 2). This is different to what has been observed when Al on GaAs(110) starts clustering during warming up of a LT deposited layer: Bonapace *et al* have reported that the surface exciton partially reappears [7]. The absence of the Ga exciton in this study thus indicates that a layer of In covalently bonded to the surface persists and that the In overlayer forms clusters by diffusing on an In monolayer rather than on the bare substrate, as in the case of RT growth. The quenching of the Ga surface exciton might be taken as
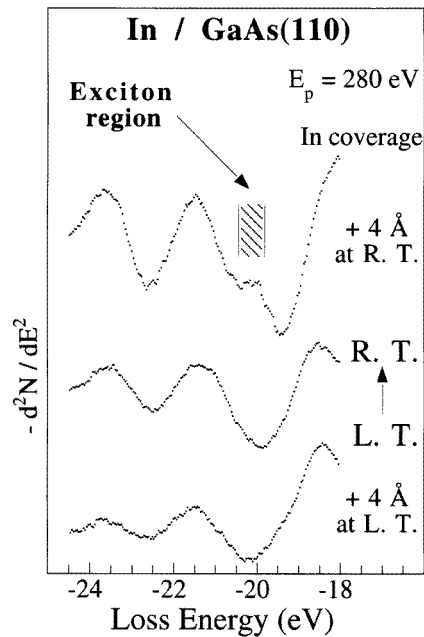
Figure 2. EELS spectra in d^2N/dE^2 form of the Ga 3d surface exciton region from 4 Å In deposited onto clean GaAs(110) at RT (top spectrum); at LT (bottom spectrum); at LT and then warmed up to RT (middle spectrum). $E_p = 280$ eV. The labels on the figure are discussed in the text.

an indication that Ga surface atoms provide the preferred sites for In adsorption. However, this *prima facie* argument turns out to be too simplistic in the light of further evidence, as we discuss below.

The photoemission experiments confirm the EELS analysis and add extra and complementary information. In figure 3 the Ga 3d–In 4d core level region is shown for the LT-grown interface, while in figure 4 As 3d core level spectra are displayed. The top spectra of figures 3 and 4 are from 4 Å In deposited directly at RT, for comparison with the spectra of LT-deposited 4 Å In subsequently warmed up to RT (second spectra from the top). The maxima in the spectra have been normalized to equal height and their energy scale is relative, taking as energy zero the kinetic energy of the bulk 5/2 component of Ga 3d, for the case of figure 3, and of As 3d in figure 4. In so doing we eliminate, for the sake of clarity, all the shifts introduced by band bending [11] and/or possible surface photovoltage effects [13–15]. The spectra have been decomposed into individual components by a line shape analysis, in which the spectra are modelled as a sum of Lorentzian doublets, with a given energy position, spin–orbit splitting and intensity ratio, broadened by Gaussians, which take into account experimental broadening effects. The line broadening induced by barrier height inhomogeneities present at the surface [16] is also considered to be Gaussian. All parameters are subjected to a least-squares optimization routine, and the fit parameters used to decompose the Ga and the As 3d core levels of the clean semiconductor are in close agreement with literature results [16].

The clean surface spectra in figures 3 and 4 are the sum of a bulk emission (b) and the emission due to surface atoms (s). After In deposition two structures related to the In 4d core levels appear in the spectra of figure 3: one feature dominates the spectra at high In coverage (m) and another one is located at 0.8 eV below it (i). We assign, in agreement
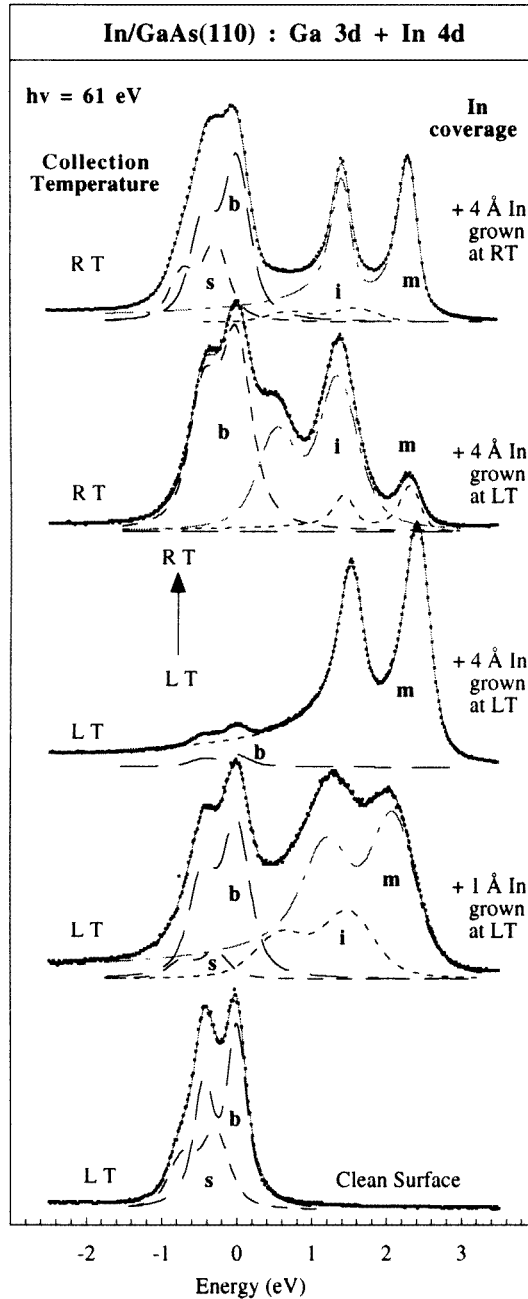
Figure 3. High-resolution core level photoemission spectra of In deposited at LT onto clean GaAs(110) as a function of nominal In coverage (bottom three curves) and after warming up to RT (second curve from top). The top spectrum is from 4 Å In deposited at RT. Kinetic energies are referenced to the Ga 3d 5/2 bulk component. Photon energy $h\nu = 61$ eV.

with previous work [5, 6], the high-energy line (m) to emission from In atoms in a metallic environment and the second In-related component (i) to In atoms bonded to the substrate.
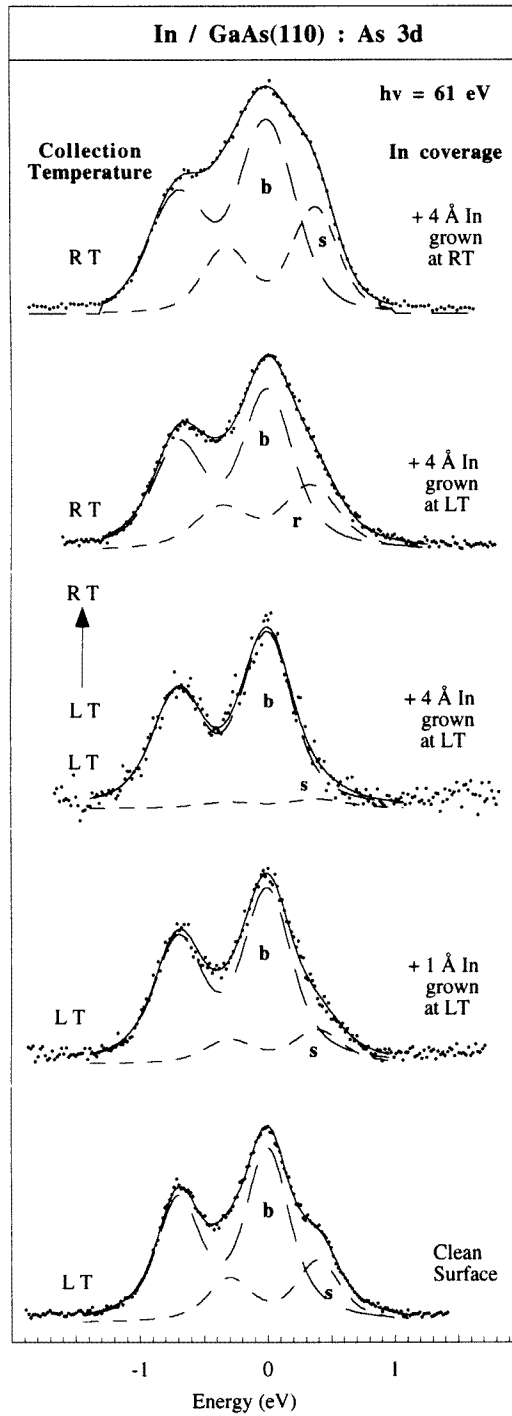
Figure 4. High-resolution As 3d core level photoemission spectra ($h\nu = 61$ eV) of In deposited at LT onto clean GaAs(110) as a function of nominal In coverage (bottom three curves) and after warming up to RT (second curve from top). The top spectrum is from 4 Å In deposited at RT. Kinetic energies are referenced to the As 3d 5/2 bulk component.

The top spectrum of figure 3 shows that at 4 Å In deposited at RT the Ga 3d component is still intense. This demonstrates the growth of metallic In clusters at RT. Moreover, the simultaneous presence of the Ga 3d surface component (and the corresponding As one in figure 4) shows the persistence of clean GaAs(110) surface regions unperturbed by In deposition. This is in agreement with the slow attenuation of the Ga 3d surface exciton measured by EELS, as discussed above.

For LT In deposition the spectra display a completely different behaviour as shown in figures 3 and 4: at 1 Å In coverage the Ga and As 3d surface components are reduced to half of their intensity on the clean surface, whereas the interfacial In component (i) (figure 3) has become half as intense as the metallic one. At 4 Å In the substrate emissions are much reduced while the surface components have disappeared completely. This confirms the quasi-laminar growth of In at LT as proposed previously [7–12] and that In covers most of the substrate surface. The presence of a metallic In component already at 1 Å coverage is consistent with the existence of a few thicker metallic indium patches, in agreement with the assumed 'Poisson-like' growth mode.

Irreversible effects are observed when LT-grown In–GaAs interfaces are annealed at RT, revealing non-equilibrium phenomena in the In overlayer growth. Figures 3 and 4 demonstrate the significant differences in the photoemission spectra between RT-annealed LT-grown interfaces and In–GaAs surfaces formed directly at RT. In figure 3 the Ga 3d bulk emission recovers high intensity after annealing but its surface component remains absent! The In interfacial component (i) becomes intense on the warmed-up interface and in the As 3d spectrum (figure 4) a new component (r) appears. The intensity and the energy position (+0.34 eV higher kinetic energy than the bulk one) of such an As 3d component cannot be associated with the surface component of the As 3d core level as observed on the spectra of the clean GaAs(110) surface and after 4 Å In deposited directly at RT (+0.4 eV higher kinetic energy than the bulk one). Instead, we ascribe it to As atoms at the surface which are covalently bonded to In. This is consistent with the absence of 'as-clean' GaAs(110) surface after RT-annealed LT-grown interfaces as shown by EELS and Ga 3d core level analysis. The low intensity of the metallic In peak (m) on the annealed surface in figure 3 is caused by the small escape depth (4–6 Å) of the photoelectrons: the quasi-laminar In film at LT will give a much higher metallic signal than a few large In islands, with low surface to bulk ratio but the same amount of material.

The photoemission results in figures 3 and 4 demonstrate the condensation of In clusters upon annealing LT-formed In–GaAs interfaces at RT, leaving parts of the substrate surface free of *metallic* In; this is also suggested by the surface exciton and the plasmon behaviour in the EELS spectra. However, the GaAs surface in between the In clusters is different to a clean unperturbed GaAs(110) surface: it is covered by a monolayer of In atoms covalently bonded to surface As atoms, at variance to the system formed by In deposition directly at RT, where the intercluster region remains uncovered by In. Our data thus indicate that the quasi-laminar In film at LT is not in equilibrium, but that the LT growth mode leads to a metastable situation as a consequence of kinetic limitations due to restricted adatom mobility at LT.

Miyano *et al* [11] have also observed in photoemission the changes in the overlayer morphology during LT to RT transition of LT-deposited In films on GaAs(110), and have suggested strong clustering upon warming, with In atoms remaining on the substrate in between the clusters. The higher resolution of our photoemission spectra and the inclusion of Ga, In, and As core level analysis in conjunction with EELS data in this work allows us, however, to establish a more detailed picture of the bonding situation at the interfaces. At first sight there appears to be an interesting conflict between the photoemission and the

EELS results: whereas the As 3d photoemission analysis in figure 4 provides conclusive evidence for In–As surface bonding, the behaviour of the Ga surface exciton in EELS seems suggestive of In attachment at Ga sites. However, the perturbation of Ga surface sites is also reflected in the photoemission spectra, namely by the absence of the Ga surface component in the spectrum of the RT-annealed surface in figure 3. Thus, both surface anion and cation sites seem to be perturbed by In adatoms. Support for either adsorption site may be found in the literature. An STM study of Au on GaAs(110) has shown preferential adsorption of Au atoms on the surface cation site [17], whereas the formation of an InAs phase on In–GaAs(110) for $T > 200\,°C$ [6] may be cited in support of In–As bonding. The indirect elimination of the cation surface exciton transition by adsorption on the anion site has also to be considered in this context. Such an indirect mechanism could, for example, be provided by an adsorbate-induced structural change of the GaAs substrate surface.

A pertinent question is why the wetting In monolayer remains on the GaAs(110) surface after LT $\rightarrow$ RT transition while it is not formed during In RT deposition. Stevens *et al* [12] have observed by LEED *I–V* analysis that the GaAs(110) surface becomes unrelaxed following In LT deposition, thereby assuming a GaAs bulk-truncated-like structure. This unrelaxation of the GaAs(110) substrate surface could trigger the indirect electronic perturbation mechanism which eliminates the Ga surface exciton transition. An In monolayer on an unrelaxed GaAs surface, once formed at LT, remains stable at RT. On the other hand, the energetic balance between individual adatom bonding and hopping at RT is clearly in favour of the formation of In clusters and islands, which provide the thermodynamically more stable system [18]. There is therefore a kinetic limitation which prevents the destruction of the LT In monolayer phase at RT, which would involve the breaking of the In–As bond and the relaxation of the substrate surface. The pseudopotential total-energy calculations for Al on Ge(100) of Batra and Circaci [19] provide some theoretical understanding of the collective stability of the In monolayer phase, once it is formed at LT. They found that one monolayer of Al of uniform coverage is strongly bound to the substrate, whereas at increased metal coverages weaker metal–substrate bonding develops, thus supporting the premise that clusters bond more weakly to the substrate than uniform monolayers [20]. A similar argument can be used, in our case, to explain why, once the quasi-laminar growth is established at LT by freezing adatom mobility on the surface, it is not removed by annealing at RT.

4. Conclusions

We have used a combination of core level photoemission and EELS to investigate the growth of In on GaAs(110) in the low-temperature to room-temperature transition to reveal the role of the kinetics in the interface formation process. We confirm that In growth on GaAs(110) is strongly temperature dependent, forming metallic clusters with unperturbed substrate surface in between at RT, and a wetting quasi-laminar phase at LT as a result of reduced In adatom mobility. The LT growth yields only a metastable phase, however, since on warming up the interface In tends to cluster. The surface so formed is significantly different from the one obtained by direct deposition of the same In quantity at RT, in that in the temperature-cycled experiments the GaAs surface remains unrelaxed and covered by an In monolayer, which is covalently bonded to As atoms of the substrate. The importance of kinetic and non-equilibrium effects resulting in irreversible morphology stages is emphasized. It is suggested that structural changes of the substrate surface, in particular the surface unrelaxation of the GaAs surface by In adsorption at LT, may be partly responsible for the stability of the LT In monolayer.

Acknowledgments

References

[1] Lüth H 1993 *Surfaces and Interfaces of Solids* vol 15 (Berlin: Springer)
[2] Mönch W 1993 *Semiconductor Surfaces and Interfaces* vol 26 (Berlin: Springer)
[3] Brillson L J 1982 *Surf. Sci. Rep.* **2** 123
[4] Argile C and Rhead G E 1989 *Surf. Sci. Rep.* **10** 277
[5] Chin K K, Kendelewicz T, Newman N, Lindau I and Spicer W E 1986 *J. Vac. Sci. Technol.* B **4** 955
[6] Cao R, Miyano K, Lindau I and Spicer W E 1990 *J. Vac. Sci. Technol.* A **8** 3460
[7] Bonapace C R, Tu W D, Li K and Kahn A 1985 *J. Vac. Sci. Technol.* B **3** 1099
[8] Savage D E and Lagally M G 1986 *J. Vac. Sci. Technol.* B **4** 943
[9] Chin K K, Kendelewicz T, McCants C, Cao R, Miyano K, Lindau I and Spicer W E 1986 *J. Vac. Sci. Technol.* A **4** 969
[10] Stiles K, Kahn A, Kilday D G and Margaritondo G 1987 *J. Vac. Sci. Technol.* B **5** 987
[11] Miyano K E, Cao R, Kendelewicz T, Lindau I and Spicer W E 1989 *J. Vac. Sci. Technol.* A **7** 731
[12] Stevens K, Soonckindt L and Kahn A 1990 *J. Vac. Sci. Technol.* A **8** 2068
[13] Alonso M, Cimino R and Horn K 1990 *Phys. Rev. Lett.* **64** 1947
[14] Hecht M H 1990 *J. Vac. Sci. Technol.* B **8** 1018
[15] Cimino R, Giarante A, Alonso M and Horn K 1992 *Appl. Surf. Sci.* **56–58** 151
[16] Cimino R, Giarante A, Horn K and Pedio M 1995 *Europhys. Lett.* **32** 601
[17] Feenstra R M 1989 *J. Vac. Sci. Technol.* B **7** 925
[18] Zunger A 1981 *Phys. Rev.* B **24** 4372
[19] Batra I P and Circaci S 1984 *Phys. Rev.* B **29** 6419
[20] Klepeis J E and Harrison W A 1989 *J. Vac. Sci. Technol.* B **7** 964