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## HREELS investigation of hydrogenated GaAs (110) surfaces

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**Abstract.** The interaction of atomic hydrogen with the cleaved GaAs (110) surface has been investigated by high-resolution electron energy loss spectroscopy (HREELS), at primary energies of 5 and 15 eV, analysing the losses associated with three different mechanisms: (i) low-energy surface collective excitations (surface TO phonon and dopant-derived free-carrier plasmon); (ii) the stretching of the Ga–H and As–H bonds; and (iii) the electronic losses above the fundamental gap, involving both surface and bulk electronic states. The first kind of loss is very sensitive to H exposure and shows that hydrogen induces a band bending at the lowest exposures. The vibrational part of the spectrum indicates that the exposure of  $10^4$  L corresponds to a coverage of one monolayer and that H binds to both Ga and As over the whole coverage range. The region of the electronic transitions indicates the disappearance of transitions of the clean surface and the appearance of new transitions characteristic of the H covered surface. At high exposures the growth of a very strong background is consistent with the presence of small metallic Ga clusters. This result is also consistent with the modifications, at the same exposures, of the low-energy region of the spectrum.

### 1. Introduction

The assumed simplicity of both hydrogen and the GaAs (110) surface stimulated different authors to study the interaction of these two systems, with the aim of understanding some fundamental aspects of chemisorption. Many surface sensitive techniques were exploited for this purpose and one of the points addressed was the knowledge of the chemisorption sites (Ga, As or both) from the lowest H coverages up to one monolayer (ML) [1–8].

Photoemission results, in particular, of both valence band [2, 5] and core-level emission [8] showed that H binds to both Ga and As. At the highest coverages some As etching occurs with the formation of a Ga-rich phase. Stronger evidence of this was achieved by some of these authors, by means of photoelectron yield spectroscopy (PYS), LEED and AES [6]. In particular, they showed that two different regimes occur in the interaction of atomic H with GaAs (110). A first adsorption regime occurs up to the onset of the first monolayer: during this stage the surface stoichiometry appears scarcely affected by H, as neither the As/Ga Auger signal ratio nor the surface plasmon change with exposure. These observations are confirmed by LEED and the only important effect seems to be a de-relaxation of the topmost atomic layer. Beyond H coverages corresponding to a little less than one monolayer, LEED shows a large disordering of the surface; the As Auger signal

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decreases faster than that of Ga; the surface plasmon disappears; the work function and the ionization energy decrease and the so-called 'black hole' effect appears in PYS [6]. The origin of all this would be a much higher reactivity of the surface to H, with the formation of clusters/islands of free Ga atoms and of AsH<sub>3</sub> (which is expected to desorb, but some of which might remain adsorbed) leaving a highly disordered surface.

Theoreticians have also faced this problem with different approaches [9–11]. Manghi and co-workers [9] determined by self-consistent pseudo-potential calculations the electronic states induced by H chemisorption in two different geometries, relaxed and ideal. They favoured the ideal one, on the basis of the experimental results of Matz and Lüth [12]. The most recent results by Bertoni and co-workers [10] and Batra and co-workers [11] indicate that, at a coverage of 1 ML, H removes the surface relaxation and induces a small counter-relaxation of the (110) surface, saturating all the dangling bonds. At 0.5 ML, H binds to both Ga and As (in agreement with experiment). As the de-relaxation involves several surface atoms around the adsorption site, at sub-monolayer coverages surface states should again be brought into the gap from the two projected bands, where they had been pushed by the complete relaxation.

Although high-resolution electron energy loss spectroscopy (HREELS) is one of the most surface-sensitive techniques for a qualitative and quantitative determination of adsorbates, to our knowledge it has scarcely been exploited for a systematic investigation of the H/GaAs(110) system [13]. Lüth and co-workers [12, 14], first reported the HREELS spectra of H and D on GaAs(110) but only at one exposure, while Chen and co-workers [15] studied the interaction of H with GaAs(110), at an exposure of 500 L, only looking at the modifications induced in the phonon-plasmon loss region. Nannarone and co-workers [16], finally, in a study of the surface anisotropy of III–V semiconductors by HREELS, reported the energy loss spectra, in the region of the electronic transitions, of GaAs(110) exposed to 1000 L of H for two surface orientations.

We have already shown in a recent paper [17] that, up to an exposure of 10<sup>4</sup> L, roughly corresponding to 1 ML in our experimental set-up, H binds to both Ga and As. In this paper we will extend the study to higher exposures, show how it is possible to deduce from the spectra an important information like the H induced band bending and study the modifications in the electronic structure induced by H, as can be obtained from the HREELS technique.

## 2. Experimental

HREELS measurements were carried out by means of a Leybold ELS 22 spectrometer mounted in a two-chamber system, with a base pressure of  $7 \times 10^{-11}$  mbar ( $7 \times 10^{-9}$  Pa), also equipped with LEED, XPS and AES techniques. Samples were GaAs(110) bars of  $5 \times 5 \times 15$  mm<sup>3</sup>, n-type Te-doped with a nominal carrier concentration of  $1.7 \times 10^{18}$  cm<sup>-3</sup>, and were cleaved along the [001] direction. Atomic hydrogen was obtained by dissociation on a Ta ribbon at 1750°C. As our data should primarily compare with those obtained by two of us (CS and FP) in Paris, the geometry was suitably chosen to approximately reproduce the same coverages with the same exposures. Exposures ranged between 10 and  $5 \times 10^5$  L (where one Langmuir, L, corresponds to one second at  $1.33 \times 10^{-6}$  mbar); they refer to the molecular hydrogen exposures, as the dissociation efficiency is not accurately known. A rough estimate of the H dose could be obtained *a posteriori* and came out to be about  $8 \times 10^{10}$  atoms cm<sup>-2</sup> L.

The primary beam energy ranged between 2–15 eV; the energy resolution was 10 meV for the measurement of the vibrational losses and 20 meV for the electronic transitions. The

angle of incidence was  $65^\circ$ , and the direction of the incidence plane was along  $[\bar{1}\bar{1}0]$ , i.e. parallel to the surface atomic chains.

### 3. Results and discussion

The HREELS technique can be exploited to investigate both the vibrational and electronic excitations of the H/GaAs system, by looking at the three different loss ranges where the effects of H adsorption are detectable.

The first one is that comprising the quasi-elastic peak and the surface collective excitations: the TO phonon (the so-called Fuchs-Kliwer phonon) and the dopant-derived free-carrier plasmon. The second region contains the losses due to the Ga-H and As-H stretching vibrations, while the third one is that encompassing the electronic transitions above the fundamental gap, and involving both surface and bulk states.

#### 3.1. Region of the surface collective excitations (0–100 meV)

In this region the surface phonon and the surface free-carrier plasmon are present. Their energies are defined, in principle, by the lattice dynamics and by the carrier concentration. However if the two excitations are not very far apart in energy (like here) they couple and the energies at which they appear are different. For the present doping concentration, the plasmon occurs at an energy higher than the phonon, and the effect of the coupling is to lower the phonon energy and to raise that of the plasmon. However the situation is even more complicated by the presence, at the very surface, of a layer of largely reduced carrier concentration where only the uncoupled phonon is present. This intrinsic layer, sometimes called 'dead layer', is *not* due to any kind of surface states but only to the boundary condition imposed on the electron wavefunction by the surface barrier [18]. Possible cleavage defects can increase the width of the depleted layer.

As a consequence, to properly describe the response of the clean sample to the incoming electrons, one has to consider it as a two-layer system (depleted layer plus bulk) with a suitable effective dielectric function.

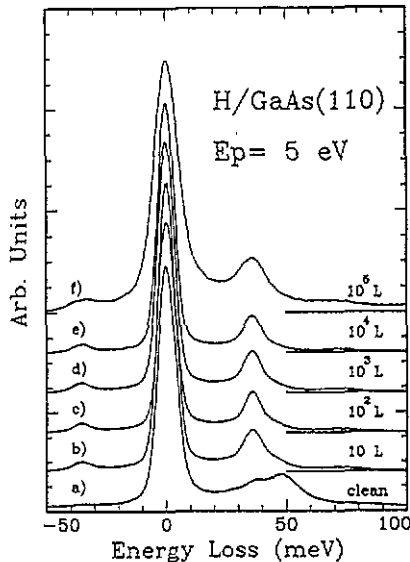
In this picture it is expected that for a layer thickness lower than the sampling depth of the incoming electrons ( $\simeq 1/q_{\parallel}$ ) three distinct features must be found: one due to the vacuum-depletion layer interface excitation and two due to the depletion-layer-bulk interface excitations.

Figure 1, curve a, shows the spectrum of the clean surface with two evident structures at  $\simeq 36$  and  $\simeq 48$  meV, corresponding to the uncoupled phonon and coupled plasmon respectively. The coupled phonon, expected at  $\simeq 27$  meV can only be inferred from the high tail of the quasi-elastic peak.

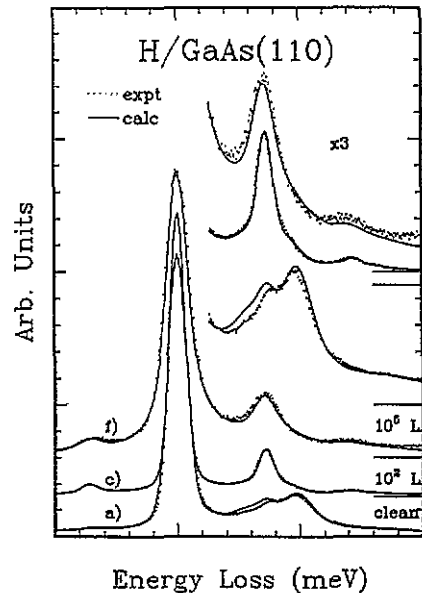
As shown by curve b, a drastic reduction of the plasmon intensity and also a shift towards lower loss energies occur after exposure to 10L of hydrogen. These results are in agreement with those of Chen and co-workers [15] and of Lüth and co-workers [14], obtained at much higher exposures.

Clearly an exposure of 10L, roughly corresponding to less than  $10^{12}$  atoms  $\text{cm}^{-2}$ , induces a band bending which largely increases the depletion layer. There follows a reduction in intensity and a shift of the two bulk-related features, while the surface phonon intensity is enhanced.

Further increases in the exposure (figure 1, curves c–f) do not further alter this loss region, apart from a reduction of the overall intensity, up to  $10^4$  L. This reduction is not apparent in figure 1 where the quasi elastic peaks have been normalized to the same height.



**Figure 1.** Energy loss spectra of the low-energy region of the clean surface, (a), and of the surface at increasing hydrogen exposures, (b)–(f). The elastic peaks have been normalized to the same height.  $E_p = 5$  eV.



**Figure 2.** Experimental curves from figure 1 (dotted) with the same reference letters: (a) clean, (c)  $10^2$  L and (f)  $10^5$  L, together with the reproduced spectra (full curves).

At  $10^5$  L the spectrum takes a different shape as the quasi-elastic peak widens and a long tail appears. Since this is the exposure at which a large increase in the surface reactivity is expected, the widening and the tail could be due to the roughening of the surface, and/or to the formation of small metallic Ga clusters [6].

However, a more complete knowledge of the surface properties of the system and of their evolution with H exposures can be obtained, from a HREELS investigation, only by reproducing as best possible each experimental spectrum with an expected spectrum calculated by introducing an effective dielectric function [19]. In the case of a layered system, this effective dielectric function  $\bar{\epsilon}(q, \omega)$  is given by

$$\bar{\epsilon}(q, \omega) = a_1 - \frac{b_1^2}{a_1 + a_2 - \frac{b_2^2}{a_2 + a_3 - \frac{b_3^2}{a_3 + a_4 - \dots}}}$$

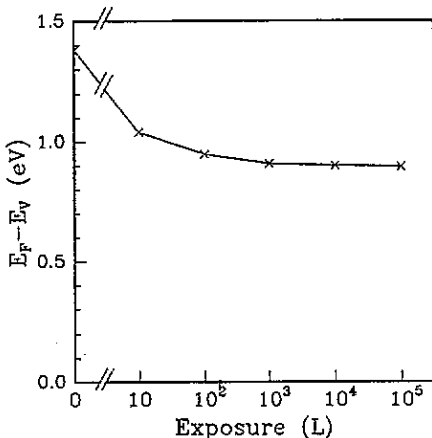
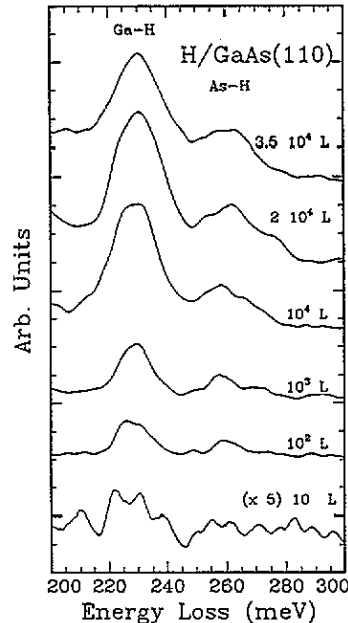
with the coefficients  $a_j = \epsilon_j(\omega) / \tanh(qd_j)$  and  $b_j = \epsilon_j(\omega) / \sinh(qd_j)$ .

By use of this model the measured spectra shown in curves a–e could be reproduced with high accuracy. The most significant examples are shown in figure 2.

This procedure was first applied to reproduce the clean spectrum, determining the bulk phonon energy  $\hbar\omega_{ph} = 33.6$  meV, the bulk plasma energy  $\hbar\omega_p = 190$  meV (corresponding to a surface screened plasmon energy  $\hbar\omega_s = 53$  meV) and the intrinsic depleted layer thickness  $d$ . In all the other spectra the only free parameter was  $d$ . The values obtained for the different exposures are listed in table 1. Hence from the Schottky expression for the voltage drop across the depletion region, the behaviour of the band bending against

**Table 1.** Depletion layer depth, as deduced from the reconstructed spectra, against  $H_2$  exposure.

Exposure (L)	Depth (Å)
0	70
10	215
$10^2$	240
$10^3$	250
$10^4$	250
$10^5$	250

**Figure 3.** Evolution with hydrogen exposure of the Fermi level position in the gap as deduced from the fitting parameters of table 1.**Figure 4.** Energy loss features associated with the Ga-H and As-H bonds stretching vibrations.

exposure could also be obtained. This behaviour is shown in figure 3 and is in very good agreement with photoyield [6] and work function measurements [7].

To fit the spectrum corresponding to  $10^5$  L a third ingredient had to be added to the model. As the possible origin of the tail is the plasmon associated with metallic Ga clusters, we included in the model a thin metallic overlayer occupying less than 10% of the total surface, whose excitation is a plasmon at about 14 eV (this is the value of Ga metal bulk plasmon [20]). The calculated spectrum is in good agreement with the experimental data, corroborating the idea of the presence of metallic islands or clusters on the heavily hydrogenated surface.

### 3.2. Region of the H stretching vibrations (200–300 meV)

Two loss peaks are detected in this energy region when atomic hydrogen is adsorbed on GaAs, as shown, for different exposures, in figure 4. The largest feature occurs at  $229 \pm 1$  meV and is attributed to the Ga-H bond stretching [12]; the smallest occurs at

$262 \pm 1$  meV. The difference with respect to the first one is 32 meV, quite different from the phonon loss (36 meV). Furthermore, the ratio between the area of the two peaks (second/first) is always about 0.50, much higher than the one between phonon and elastic peak (0.16). Therefore we conclude that on the (110) GaAs surface the peak at 262 meV must be attributed to the As-H stretching and not to a double loss, i.e. to the excitation of the Ga-H stretching plus phonon, as proposed for other surfaces [21].

Figure 5 shows the area of the two peaks against exposure up to  $1 \times 10^5$  L. After an increase for very low exposures, faster than a linear one, there is a saturation at  $10^4$  L, which we take as indication that, in our set-up, this exposure corresponds to a coverage of one monolayer, as in the experiments made in Paris. As already stated, the ratio between the intensities of the Ga-H and As-H vibrations is always about two, confirming that from the lowest exposures H binds to both Ga and As.

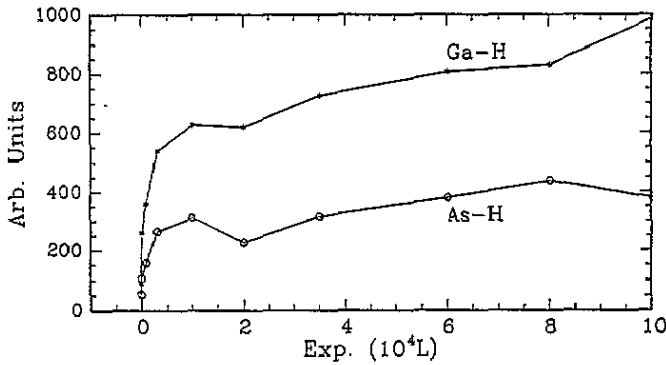


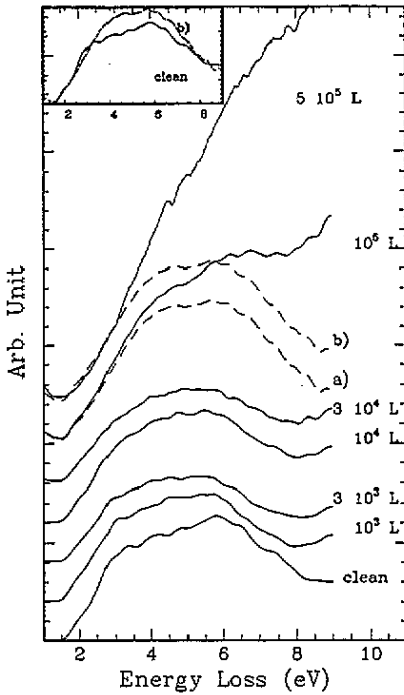
Figure 5. Intensity of the Ga-H and As-H stretching losses at increasing exposures. The plateau at  $10^4$  L marks the completion of the first monolayer.

### 3.3. Electronic transitions (1–9 eV)

The energy loss spectra due to the transitions above the fundamental gap of GaAs are shown in figure 6. The lower curve refers to the clean surface and is in perfect agreement with previous results [22], while the other curves show the effect of increasing H exposures. All the spectra were normalized to the total area of the spectrum to account for the large tail of the quasi-elastic peak occurring at exposures larger than  $10^4$  L. The lowest exposure introduced for this part of the study was 500 L.

The origin of the different features for the clean surface was determined on the basis of their energy and azimuthal dependence by del Pennino and co-workers [22]. The main features at 2.9, 3.4 and 4.9 eV were attributed to transitions between purely bulk states, that at 1.9 eV to a transition between bulk and surface states, while those at 2.6 and 3.9 eV to transitions between states of completely surface character.

The interaction of hydrogen induces changes in the spectra. For instance, after 500 and  $10^3$  L, the feature around 1.9 eV appears enhanced, and a new structure can be clearly seen around 3 eV. Other small but distinct peaks are observed around 3.7, 4.5, 5.3 in particular, whereas most of the clean surface features are no longer observable. It is difficult to follow such small features in the spectra as the hydrogen dose increases because the absolute intensity decreases and they may be hidden in a relatively larger noise level. Thus,



**Figure 6.** Losses associated with the electronic transitions between surface and/or bulk states at increasing exposures. Curves (a) and (b) correspond to the spectra of  $10^3$  L and  $5 \times 10^5$  L, after subtraction of a 'plasmon' at higher energy. Inset: comparison between the spectrum of the clean surface and curve (b),  $5 \times 10^5$  L.  $E_p = 15$  eV.

beyond  $10^3$  L, the small wiggles in the spectra are probably not significant. It is difficult to compare our spectra on hydrogenated GaAs to the spectrum reported by Nannarone and co-workers [16] after a  $10^3$  L exposure to hydrogen since even their clean surface spectrum is quite different from ours and from that of Froitzheim and Ibach [23].

We did not try to directly identify the transitions giving rise to the features observed at the lowest doses because of the complexity of the H-induced effects. We can safely state, however, that they involve the quenching of the clean surface states, the appearance of new surface states (characteristic of the H-covered surface [9]) and modifications of the transitions on the remaining clean parts of the surface. Besides changes in the features, the spectra show a regular evolution up to  $3 \times 10^4$  L with a decreasing relative intensity and a very slightly increasing background. In figure 7, the difference spectrum (clean-H covered) is shown for the one-monolayer case ( $10^4$  L). Because of the smoothing effect deriving from the higher noise-signal ratio at the dose considered, this curve enhances the clean surface structures which appear as peaks, and puts into evidence only the broader H-induced effects.

The H-covered spectrum has an overall smaller intensity except in the gap region ( $\Delta E < 2$  eV) where a new feature at 1.65 eV and an enhanced structure around 2 eV are observed. This indicates that new states are induced at the top of the valence band and that some of them penetrate into the gap, so that new transitions, at lower energies, can occur. As a result, the edge of the transitions is lowered by about 120 meV. This is consistent with the PYS measurements of M'hamedi and co-workers [6] which showed that the effective density of filled states increases with hydrogenation just below the top of the valence band and that the tail of this distribution enters into the gap. The difference spectrum of figure 7 is in very good agreement with the differential reflectivity spectrum ( $\Delta R/R$ ), in the range 0–4 eV, obtained by subtracting from the clean surface reflectivity that of the sample covered by one monolayer of H, measured by Chiaradia and co-workers [24]



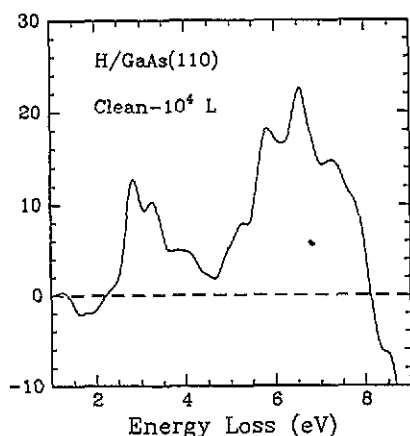


Figure 7. Difference spectrum between the clean spectrum and that of  $10^4$  L.

and calculated by Manghi and co-workers [25]. In that case a small dip at about 1.8 eV marks the appearance of new states inside the gap, while positive peaks at about 2.7, 3.3 and 3.6 eV show the reduction of bulk-related transitions, induced by hydrogen adsorption.

The overall decrease observed above 2 eV is not uniform (figure 7). It appears stronger in the loss regions between 2–4 eV, and between 6–8 eV. The former is consistent with the calculations of Manghi and co-workers [9,26], for the coverage of 1 ML, showing that both filled and empty surface states induced by H are farther away from the band edges than those of the clean surface. It agrees also with photoemission results giving information on the filled initial states possibly coinvolved in the transitions detected by HREELS and showing, below 1 ML, a decrease in the emission from the valence band between its top and -3 eV [5,27].

A drastic change in the spectrum shape occurs at the exposure of  $10^5$  L. Here a strongly sloping background affects the spectrum. This background is still increased at  $5 \times 10^5$  L, where it dominates the spectrum (see the upper curve in figure 6). After  $10^5$  L, one notices two broad structures centred at about 4.5 and 6 eV emerging from the high background. Given the fit to the low-energy part of the spectrum for corresponding exposures, one can argue that the sloping part is just the tail of the plasmon loss occurring in the small Ga clusters, formed after the strong reaction of the surface with hydrogen. With this idea in mind, we subtracted from both spectra a Gaussian centred at about 14 eV (energy of the bulk plasmon of metallic Ga), with quite a large halfwidth (due to the cluster dimensions the plasmon should be strongly damped) and with increasing intensity in going from  $10^5$  to  $5 \times 10^5$  L. The broken curves a and b in figure 6 show the two spectra after the subtraction. These curves appear fairly similar to those obtained at lower exposures, encompassing the same loss energy range, with an intensity which is reduced between 2–3.2 eV and enhanced above the latter, particularly at  $5 \times 10^5$  L. This is shown in the inset of figure 6 where the clean spectrum is compared with the one corresponding to the highest exposure, after 'Ga-plasmon' subtraction.

The decrease also observed at lower loss energies at these large exposures is consistent with the reduction of the emission within about 3 eV from the valence band maximum, as evidenced by photoemission measurements performed beyond the 1 ML coverage range [8,27]. In those studies an increase of emission is also observed below -4 eV, with two new peaks at about -5.5 and -8.5 eV. At the highest exposures, lower than ours, a Ga enrichment was evident but without the clear indication of truly metallic gallium from either the valence band or the core lines emission. These results are compatible with ours. In particular, in the high exposure range, the broad loss feature we observe around 6 eV

could be related to transitions between the states giving rise to the (broad) structure around 5.5 eV in photoemission and the bottom of the conduction band. These states have been related [8] to new Ga-H hybrid features on the basis of calculations performed for 1 ML coverage. However, other calculations [28] performed on GaAs surfaces terminated by dihydrides, GaH<sub>2</sub> or AsH<sub>2</sub>, lead to an electronic density of states at about 5 eV below the valence band edge in the case of H bonding to As.

Therefore, from all the above results, it is reasonable to make the following two statements.

(i) In the early stages of interaction with H up to 1 ML, the electronic transitions below 4 eV are depressed, with the exception of the small loss feature at an energy below the gap. The latter should correspond to transitions from the new low density of states (probably at the  $\bar{\Gamma}$  point of the surface Brillouin zone [26]) only detectable with the highly sensitive PYS [6], to the bottom of the conduction band.

(ii) At the higher exposures, the loss spectra undergo a dramatic change due to the presence of an intense background with a steep slope. It is appealing to justify this background as due to the tail of a high-energy plasmon, occurring in small metallic Ga islands. Once this background is subtracted, the spectra clearly show two broad features roughly centred at 4.5 and 6 eV. These are most likely related to hydrogenated species which are present on the surface.

#### 4. Conclusions

Three different signatures of the hydrogen interaction with GaAs can be detected by HREELS.

By far the most sensitive are the modifications in intensity and energy position of the losses associated with the surface phonon (Fuchs-Kliewer) and to the free carrier surface plasmon, in the 0–100 meV loss range. These modifications are due to the sensitivity of the technique to the build-up of a depletion layer, caused by the charge trapped in the electronic states associated with a small number of surface defects induced by hydrogen. By the use of a suitable model the spectra can be reproduced and the depletion layer thickness determined. From this the band bending can also be estimated. Above 10<sup>5</sup> L a relevant change in the spectrum shape can be justified by assuming the presence, on less than ten per cent of the total area, of metallic islands able to sustain a high-energy plasmon.

With less sensitivity, the energy loss signal associated with the stretching vibrations of the Ga-H and As-H bonds (between 200 and 300 meV) give an indication of the number of H atoms interacting with the surface. The intensity of these two signals reaches a plateau at about 10<sup>4</sup> L confirming that (in our experimental set-up) this exposure corresponds to the completion of the first monolayer. Above this value a first decrease suggests the beginning of some disruptive reaction involving also inner layers. The ratio between the Ga-H and As-H intensities is always about two, again confirming that H binds to both Ga and As from the lowest exposures.

Finally, starting from intermediate exposures, the low-intensity electronic transitions (in the 1.5–9 eV range) also show important changes, connected to the modifications of the filled and empty surface states distribution induced by hydrogen. A first overall reduction in intensity below 1 ML, is followed by an increase above 1 ML. At very high exposures, a strongly sloping background affects this part of the spectrum. The explanation invoked, in this exposure range, for the low-energy part of the spectrum has been applied here also. Thus, assuming the presence of small metallic islands sustaining a plasmon at about 14 eV (as in bulk Ga) the shape of the spectra can be completely justified.

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