

## Reflection electron-energy-loss investigation of the H-GaAs(110) surface

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Reflection energy-loss spectra have been performed on GaAs(110):H system at several stages of coverages. The fully chemisorbed surface shows several H-induced losses. They have been interpreted on the basis of hydride electronic structure and of self-consistent pseudopotential calculations. The results indicate that chemisorption takes place on both Ga and As sites of the unrelaxed substrate through covalent directional bonds.

### I. INTRODUCTION

This paper deals with the electronic properties of the GaAs(110) surface in the presence of chemisorbed hydrogen. We present new reflection electron energy-loss spectra (REELS) through which it is possible to gain information about the chemisorption bond between hydrogen and surface atoms.

This system has been recently investigated by high-resolution energy-loss spectroscopy<sup>1</sup> to detect vibrational modes associated with the chemisorbed species. Both H—Ga and H—As stretching modes have been observed and such experimental finding has allowed to conclude that hydrogen chemisorbs on both Ga and As sites.

Recently theoretical work<sup>2</sup> on the same system has indicated the possibility of discriminating between different chemisorption models through the analysis of the H-induced features in the electronic spectrum. To this end a detailed experimental study of the modifications of the electronic structure caused by the chemisorption is needed. Such an investigation has not been attempted up to now, although some important aspects, like the effects of the chemisorption on the values of the work function and the threshold energies, have been pointed out by previous photoemission results.<sup>3</sup>

The analysis of the REELS spectra seems particularly promising to clarify the nature of the chemisorption for two reasons. First, REELS spectra are extremely sensitive to variations of the chemical environment of surface atoms. Second, the electronic properties of the clean surface have been thoroughly investigated and reliable assignments of the main structures of the loss spectrum have been done.<sup>4</sup>

We have therefore performed a careful study of the loss spectra of GaAs(110) at different H coverages with the purpose of achieving information on the electronic properties of the chemisorbed phase and on the configurations of the semiconductor surface atoms after chemisorption. This paper is devoted to the presentation of these spectra and to their comparison with the available theoretical work.

### II. EXPERIMENT AND RESULTS

The clean GaAs(110) surface has been cleaved in ultrahigh vacuum (UHV) at a base pressure of  $10^{-10}$  Torr ( $1.33 \times 10^{-8}$  Pa). The cleaved surface displayed a very good low electron energy diffraction (LEED) pattern, typical of the  $(1 \times 1)$  surface structure.

Atomic hydrogen exposures have been obtained by flushing molecular hydrogen in the vacuum chamber at  $5 \times 10^{-5}$  Torr in presence of hot (2000 K) tungsten filament. Several geometries have been attempted to optimize the dissociation rate of the  $H_2$  molecules.<sup>5</sup> The filament was not in line of sight with the sample surface, and the saturation coverage occurred after an exposure of about  $10^3$ – $10^5$  langmuirs ( $1 \text{ L} \equiv 10^{-6}$  Torr sec) depending on the experimental set up. A monolayer coverage has been assumed when the surface features of the clean surface were completely disappeared from the REELS spectra.

Partial coverages have been achieved either by partial exposures or by desorbing hydrogen through heating cycles. Several minutes at about 350 °C have been sufficient to remove the adsorbed atoms and to restore the REELS spectra of the clean surface.

The LEED pattern is never affected by atomic hydro-

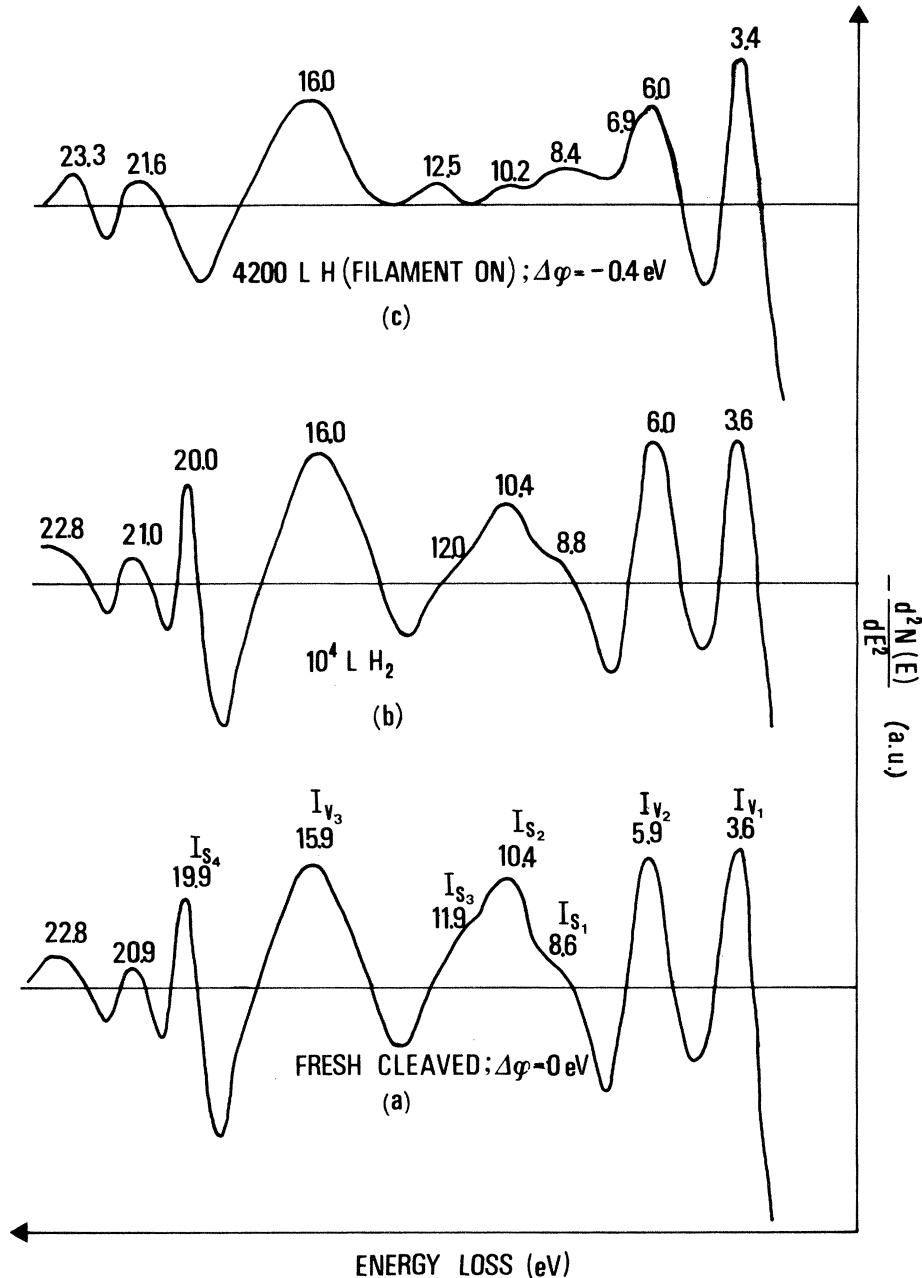


FIG. 1. REELS spectra taken in the second-derivative mode at primary beam energy  $E_p = 100$  eV on (a) fresh-cleaved GaAs(110) surface, (b) GaAs(110) surface after an exposure of  $10^4$  L of molecular hydrogen, and (c) GaAs(110) surface after an exposure of 4200 L of atomic hydrogen.

gen exposures either in number or position of the spots. Thus, the symmetry of the GaAs(110):H surface does not change and hydrogen-induced modifications, if any, should be looked for by an intensity analysis of the spots.

The surface cleanliness has been checked after each run by the Auger-electron spectroscopy (AES) while the gas purity has been controlled by a mass spectrometer. The loss measurements have been performed with a Varian Associates single-pass cylindrical mirror analyzer (CMA) with a coaxial electron gun. The spectra have been recorded driving the analyzer in the second-derivative

mode. A peak-to-peak modulation of 1 V has been used. The CMA energy window was about 1 eV because the primary beam energy was always about 100 eV.

The REELS results are reported in Figs. 1–3. The chemisorption effect of atomic hydrogen at saturation coverage can be understood comparing curves (a) and (c) of Fig. 1. Curve (c) should be a genuine spectrum of the GaAs(110):H system since exposures at partial pressures of molecular hydrogen do not affect the fresh cleaved GaAs(110) surface [Fig. 1(b)].

Figure 2 shows the evolution of the structure at  $\sim 19.9$

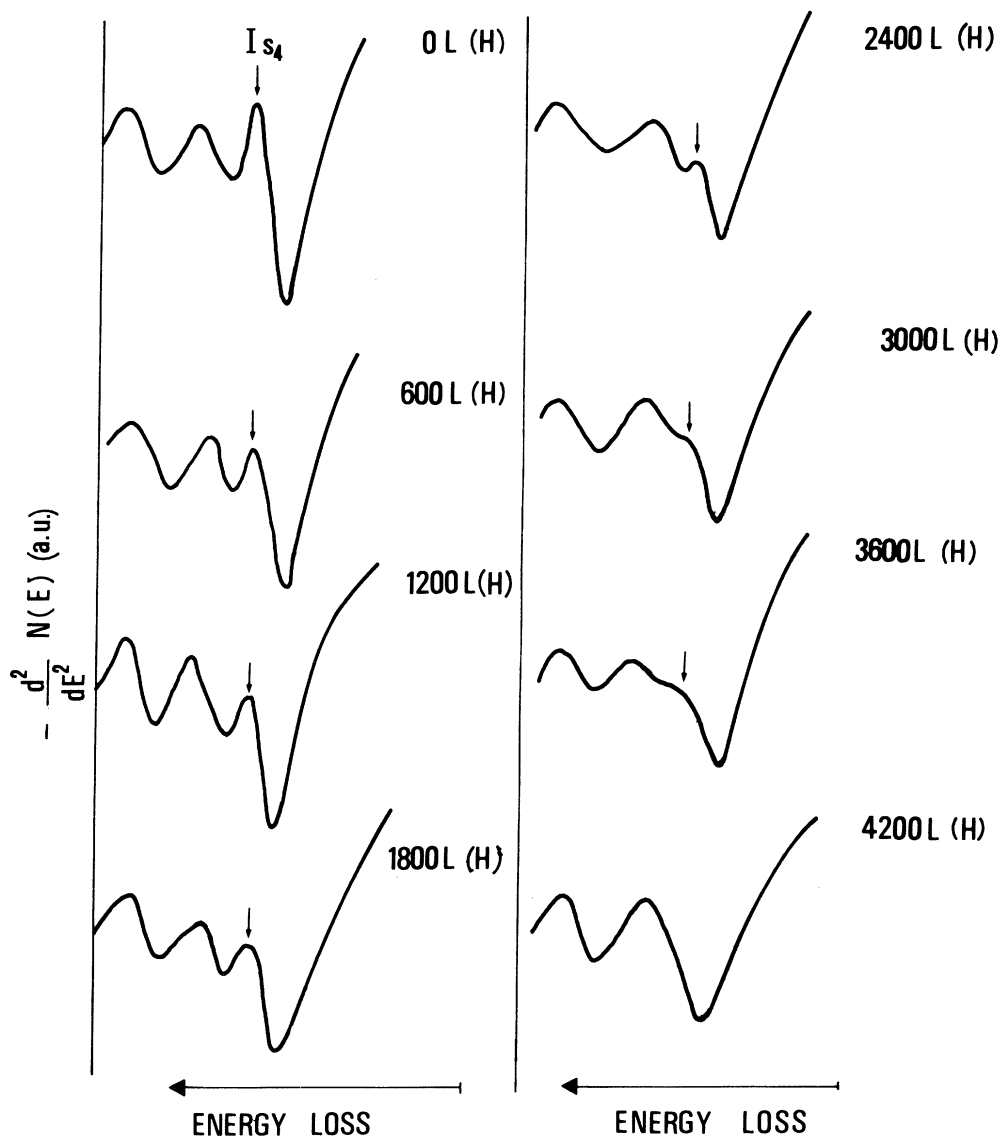


FIG. 2. Evolution of the surface exciton with H coverage.

eV with different H coverages. It can be used to monitor the saturation coverage because it disappears without changing its excitation energy when the H monolayer is built up.

Figure 3, instead, summarizes the effect of H desorption through successive heating cycles on the heavy H-covered surface. This figure should be read following the arrows, which indicate the sequence of heating cycles starting from the fully chemisorbed surface. The evolution of each structure helps to discriminate the nature of the corresponding excitation. The features which are not affected by hydrogen (i.e.,  $I_{V_1}$ ,  $I_{V_2}$ , and  $I_{V_3}$ ) have bulk character, while the surfacelike excitations (i.e.,  $I_{S_1}$ ,  $I_{S_2}$ , and  $I_{S_4}$ ) should be very sensitive to chemisorbed species and indeed they disappear gradually with atomic hydrogen coverage up to saturation where they are completely absent. They depend, in fact, on the electronic structure

of the unsaturated dangling bonds of the cleaved GaAs(110) surface.<sup>4</sup>

The features at about 8.4, 10.2, and 12.5 eV of H-covered surface [Figs. 1(c) and 3(e)] are, therefore, H induced. The loss of 10.2 eV occurs at the same energy of the  $I_{S_2}$  excitation and could still have memory of  $I_{S_2}$  but the intensity evolution versus H desorption rules out this possibility and supports, instead, the H-induced nature.

Relative changes of the GaAs(110) work function have been measured with respect to the analyzer work function, which in turn has been assumed to remain constant. To this purpose, the sample has been negatively biased and an ultraviolet photon beam ( $\hbar\omega = 21$  eV) has been focused on it. Then the secondary electron region of the energy distribution curve (EDC) has been accurately recorded versus H exposure. The shifts of the zero crossing of EDC's give directly the change of the sample work function with

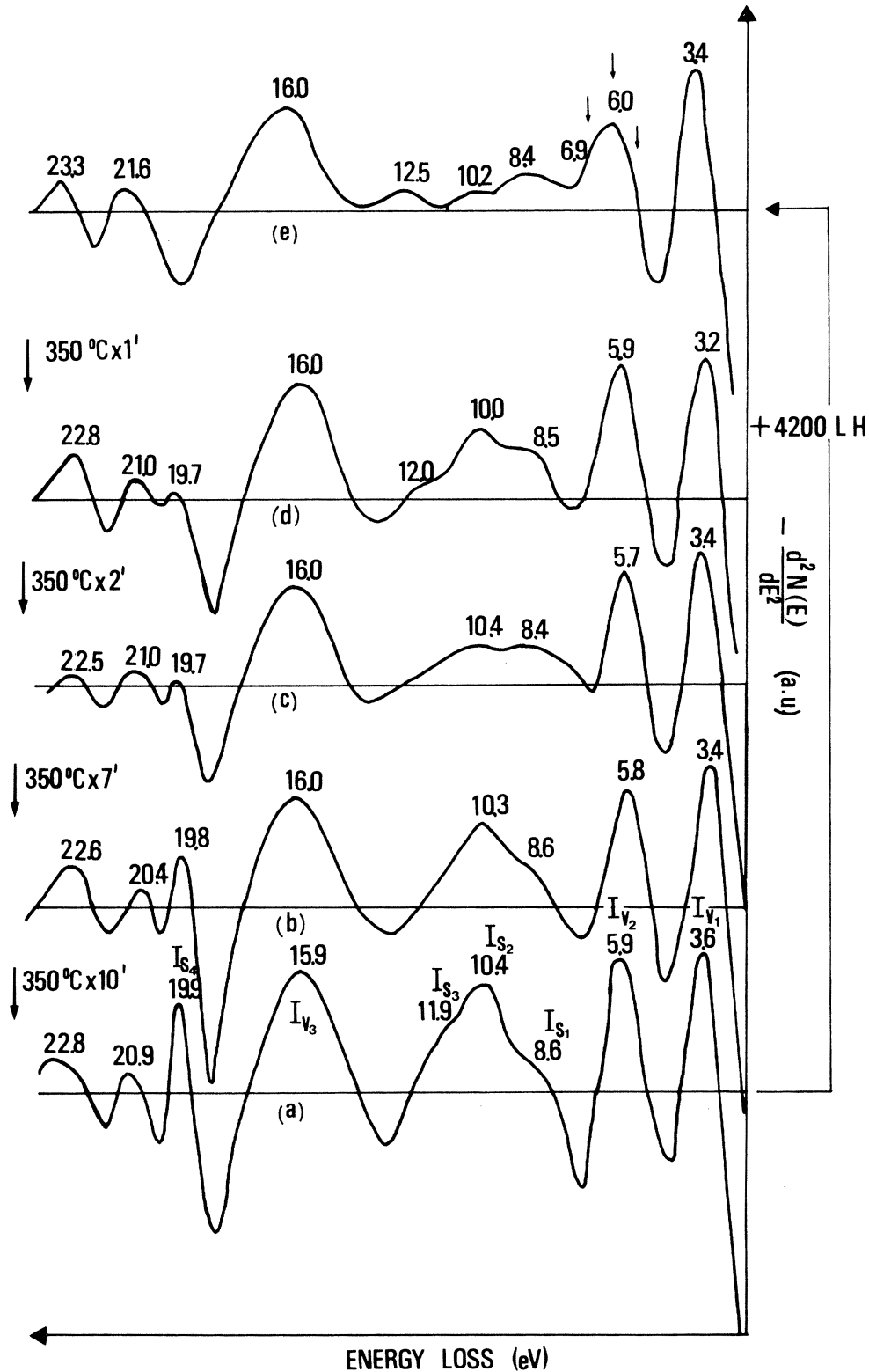


FIG. 3. Effect of H deposition on GaAs(110):H system. Arrows indicate sequence of the heating cycles starting from the heavy H covered GaAs(110) surface.

respect to the analyzer.

Figure 4 shows the behavior of the relative change  $\Delta\phi$  of the GaAs(110):H work function versus H coverage. Although it is dependent on the relative position between the

hot filament and the sample surface, and, therefore, the energy-loss data cannot be labeled by means of this more reliable parameter, the monolayer coverage occurs with high reproducibility at the same value:  $\Delta\phi = -0.4$  eV.

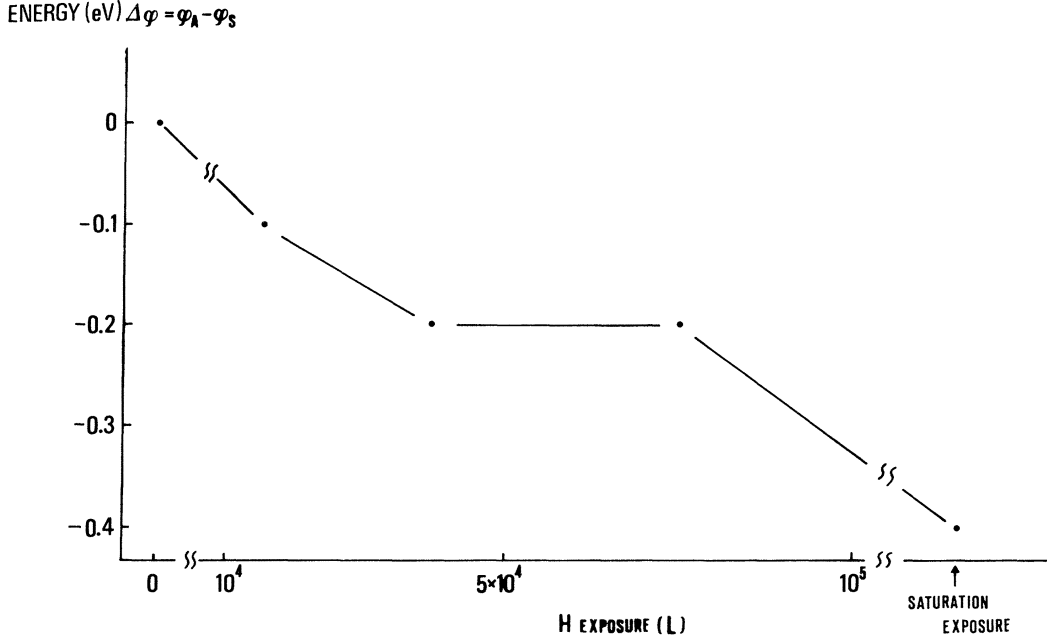


FIG. 4. Behavior of the relative change  $\Delta\varphi$  of the GaAs(110):H work function vs H coverage. ( $\Delta\varphi=0$ : fresh-cleaved surface;  $\Delta\varphi=-0.4$  eV: fully covered surface.) The Ga 3d surface exciton has been used to monitor the H coverage. It disappears completely when an H monolayer is built up on the GaAs(110) surface.

At this coverage stage, the surface exciton ( $\sim 19.9$  eV) completely disappears, as shown in Figs. 1–3.

This result is confirmed by partial yield measurements performed on the same sample and in the same experimental apparatus. All of that rules out any change of contamination effects induced by the electron beam.<sup>6</sup>

### III. INTERPRETATION SCHEME OF REELS SPECTRA

As it is well known,<sup>7</sup> any REELS spectrum is a superposition of a number of contributions coming from inelastic scattering processes which occur in the bulk or near the solid-vacuum interface. The excitation probability for a volume loss is proportional to the volume loss function (VLF):  $-\text{Im}[1/\tilde{\epsilon}_L^V(\omega)]$  where  $\tilde{\epsilon}_L^V(\omega)$  is the complex longitudinal dielectric function of the solid. The losses  $I_{V_1}$ ,  $I_{V_2}$ , and  $I_{V_3}$  [Fig. 1(a)] of the fresh-cleaved GaAs(110) surface are due to volume inelastic processes. They occur at the energies where the complex equation  $\tilde{\epsilon}_L^V(\omega)=0$  is satisfied. In this case, in fact, electron collective oscillations are built up in the sample.  $I_{V_1}$  and  $I_{V_2}$  collective excitations are highly damped by the near interband transitions, while  $I_{V_3}$  is the main plasmon which occurs in the free-electron metallic region of the semiconductor.

The losses  $I_{S_1}$ ,  $I_{S_2}$ , and  $I_{S_3}$  have been assigned<sup>4</sup> as surface losses since all of them are due to scattering processes occurring at the interface region between solid and vacuum. They are strongly dependent on the electronic charge distribution of the topmost layer of the sample surface although the electronic origin of  $I_{S_1}$  and  $I_{S_3}$  is different from  $I_{S_2}$ .  $I_{S_1}$  and  $I_{S_3}$ , in fact, keep existing only until the saturation of dangling bonds. The excitation probability

for an interface loss is proportional to

$$-\text{Im} \frac{1}{\tilde{F}(\omega)}, \quad (1)$$

where  $\tilde{F}(\omega)$  determines the longitudinal-mode equation  $\tilde{F}(\omega)=0$  of the three media (vacuum, surface layer, bulk) “experienced” by the electron probe.<sup>8,9</sup> Assuming sharp interfaces (boundary planes), the eigenvalue-mode equation of a system of two semi-infinite media (vacuum and GaAs bulk substrate) separated by a layer (the surface layer of GaAs) of thickness  $d$  and dielectric function  $\tilde{\epsilon}_L^S(\omega)$  is given<sup>10</sup> by

$$\tilde{F}(\omega, q_{\parallel}, d) = 1 + \left[ \tilde{\epsilon}_L^S(\omega) \frac{1 - e^{-2q_{\parallel}d}}{1 + e^{-2q_{\parallel}d}} \right], \quad (2)$$

where

$$\Delta = \frac{\tilde{\epsilon}_L^S(\omega) - \tilde{\epsilon}_L^V(\omega)}{\tilde{\epsilon}_L^S(\omega) + \tilde{\epsilon}_L^V(\omega)}$$

and  $q_{\parallel}$  is the exchanged wave vector parallel to the interface planes. The term in the large parentheses has the meaning of an effective dielectric constant of the GaAs(110):H system.

Interface collective excitations occur at the energy values where Eq. (2) is satisfied, implying several consequences.<sup>8,9</sup> The most important and general aspect is that, at least in the valence-band region (0–18 eV), it is not correct to interpret the surface features of a REELS spectrum in terms of structures of only  $\tilde{\epsilon}_L^S(\omega)$  because of the boundary-condition effects at the interface. Moreover, any correlation between the electronic band structure and the REELS data should be done cautiously. In the simple

case of a semi-infinite medium it is possible to show<sup>11</sup> that a one-to-one correspondence exists between transverse and longitudinal frequencies. Instead, when interface studies are performed, the correspondence may not occur. Boundary-condition effects mix the electronic properties of bulk and surface, and the interpretation of interface REELS data in terms of band-structure calculations, i.e., in terms of transverse frequencies, should require a proper analysis of Eq. (2) following the interpretation scheme appeared in Ref. 8.

Keeping these aspects in mind we will associate the losses to specific transitions on the basis of the present knowledge on the electronic structure of molecular hydrides and by comparison with the outcome of self-consistent pseudopotential calculations.

#### IV. DISCUSSION

##### A. Expected interband transitions

Since neither Ga nor As give rise to molecular hydrides in a tetrahedral configuration, one can try to gain some understanding of the electronic structure of chemisorbed hydrogens by analyzing the molecular energy levels of GeH<sub>4</sub>. The valence-energy levels of this molecule are known from x-ray photoemission experiments.<sup>12,13</sup> Two occupied levels are found at  $-18.5$  and  $-12.3$  eV with respect to the vacuum level, which correspond to  $a_1^+$  and  $t_2^+$  energy states, respectively. For group-IV hydrides these orbitals are analogous to the  $s$  and  $p$  orbitals of their respective united atoms. In particular, the  $a_1^+$  state has a dominant contribution from Ge  $s$  orbitals, while  $t_2^+$  arises from bonding combinations of Ge  $p$  states with the hydrogen  $s$  orbitals. The valence states of group-V hydrides, like AsH<sub>3</sub> and PH<sub>3</sub>, have a similar behavior.<sup>14</sup> In this case

the  $a_1$  state has mainly As  $s$  character, while the doubly degenerate  $e$  state arises from As  $p$  orbitals combined with hydrogens. It is interesting to notice that the binding energies of these levels, as measured in photoemission, are close to the values found for GeH<sub>4</sub>, being, respectively, 19 eV for  $a_1$  and 12.7 eV for  $e$ . We can therefore take the values for GeH<sub>4</sub> as typical values for the orbital energies of the molecular states arising from H bonding with Ga and As atoms.

As to the unoccupied valence states, they can be derived for GeH<sub>4</sub> from theoretical calculations.<sup>15</sup> The estimated energies are  $-4.95$  eV for  $a_1^-$  and  $-5.2$  eV for the triply degenerate  $t_2^-$  state.

A similar picture for chemisorbed H states emerges from the results of self-consistent pseudopotential calculations for H deposited onto GaAs(110).<sup>2</sup> Figure 5 reports the results of such a calculation obtained by considering H chemisorption on both Ga and As sites of the unrelaxed semiconductor surface. Hydrogen-induced states are indicated by H<sub>*i*</sub>, while A<sub>*i*</sub> and C<sub>*i*</sub> label the anion and cation surface states of the substrate, which are not modified by the chemisorption process. Details of the calculations have been published elsewhere.<sup>2</sup>

There are four main bands which show a significant H contribution. Among them, those labeled H<sub>1</sub> and H<sub>4</sub> arise from combinations of As states with hydrogens, H<sub>1</sub> being mostly As  $s$  like, while H<sub>4</sub> shows a large As  $p$ -like contribution. Similarly state H<sub>2</sub> (H<sub>5</sub>) has a large  $s$  ( $p$ ) Ga character. State H<sub>3</sub> is a resonance due to Ga  $s$  states and exists only in the proximity of the  $\bar{M}$  point of the two-dimensional Brillouin zone. We see therefore that for every surface atom the theory predicts a couple of chemisorption induced states, having a character similar to the occupied states of the hydrides. The location in energy of these hydrogen induced features is consistent with the ex-

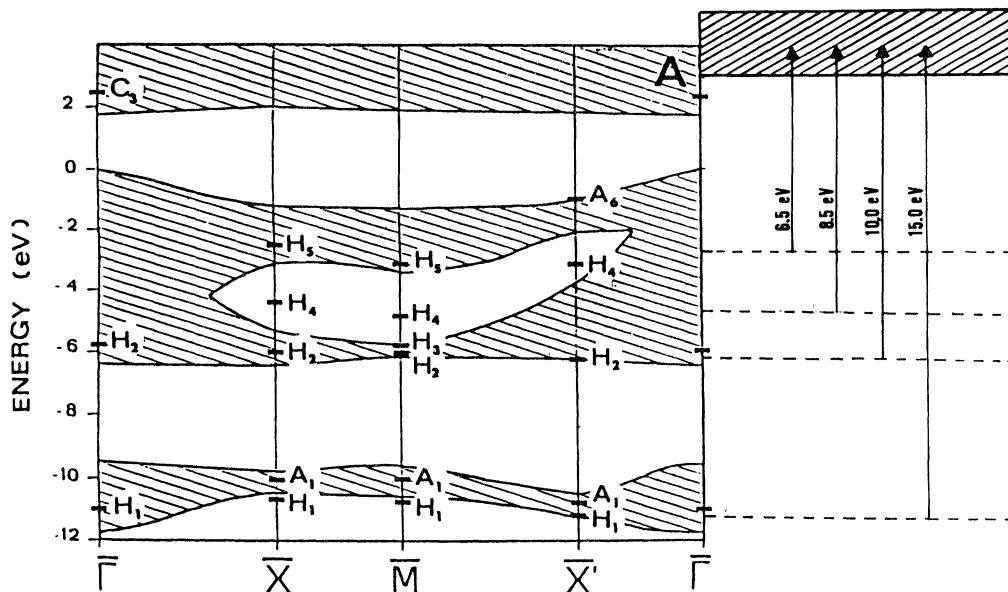


FIG. 5. Self-consistent pseudopotential calculations for H deposited onto GaAs(110) unrelaxed surface (Ref. 2). Arrows show the expected interband transitions starting from hydrogen-induced states. Final H-induced bands lie in the energy range between 3–5 eV above the valence-band maximum (Ref. 17).

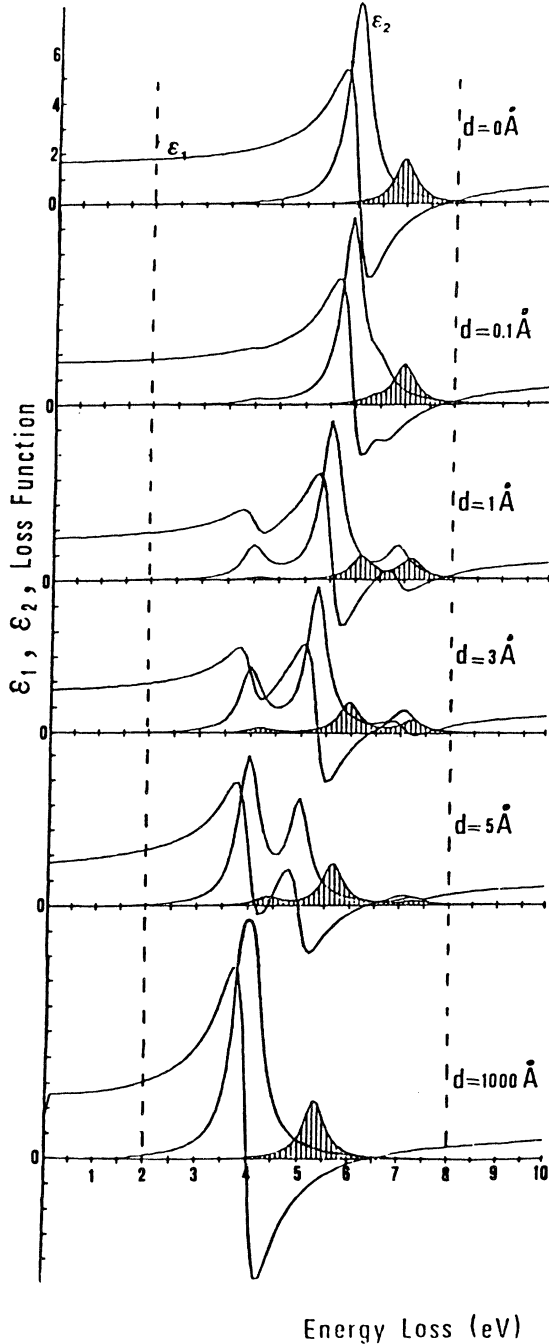


FIG. 6. Phenomenological model<sup>8</sup> which reproduces the surface-loss function (hatched area) of the three-media system (vacuum, surface layer, bulk) "seen" by the electron probe. Real and imaginary parts of the dielectric constant are shown. In the intermediate range ( $d > 0 \text{ \AA}$ ;  $d < 1000 \text{ \AA}$ ) they represent the effective dielectric constant [see Eq. (2)]. The parameter  $d$  simulates the thickness of the surface layer. The transverse frequencies of the surface and bulk oscillators are  $\omega_T^S = 4 \text{ eV}$  and  $\omega_T^V = 6 \text{ eV}$ , respectively, while the correspondent longitudinal frequencies are  $\omega_L^S = 6.4 \text{ eV}$  and  $\omega_L^V = 7.8 \text{ eV}$ . In the limiting cases the losses are localized by the surface longitudinal frequencies:  $\omega_{LS}^S = 5.4 \text{ eV}$  ( $d = 1000 \text{ \AA}$ ) and  $\omega_{LS}^V = 7 \text{ eV}$  ( $d = 0 \text{ \AA}$ ) (Ref. 8). The full width at half maximum of the two oscillators are taken equal:  $\Gamma = 0.5 \text{ eV}$ .

perimental findings for the hydrides.  $H_1$  lies  $\sim 11 \text{ eV}$  below the valence-band maximum (approximately  $18 \text{ eV}$  below the calculated vacuum level) and is separated from  $H_4$  by  $\sim 6 \text{ eV}$ , as found in  $\text{AsH}_3$  and  $\text{GeH}_4$ . The bands arising from bonding between hydrogens and Ga atoms are somewhat higher in energy, being located around  $-6 \text{ eV}$  ( $H_2$ ) and  $-3 \text{ eV}$  ( $H_5$ ) from the valence-band maximum. This difference can be easily accounted for by noticing that the initial energies of  $s$  and  $p$  states are higher in Ga atom than in As.<sup>16</sup> A similar trend, but in the opposite direction, is found in the measured ionization potentials comparing from group-V to -VI hydrides.<sup>14</sup>

To single out the possible final states of electron excitations and then the transverse frequency we have to look at the unoccupied valence levels. The pseudopotential calculations indicate that empty H-induced features in the energy range between  $3\text{--}5 \text{ eV}$  above the valence-band maximum.<sup>17</sup> The origin of these states is essentially the same as that for the hydrides: They arise from antibonding combinations of  $s$  or  $p$  states of the atom under consideration with the hydrogen orbitals. Their energy location is close to the theoretical values for  $\text{GeH}_4$ . However, due to the coupling with the continuum of the bulk states, they have a resonant character, i.e., they show a significant dispersion energy and are considerably less localized than the filled H-induced states. It seems reasonable to identify these empty states as final states of the electron excitations associated with the H-induced losses.

Figure 5 shows the scheme of the electronic transitions derived from the band-structure-calculations. The transitions occur at about  $6.5, 8.5, 10.0,$  and  $15.0 \text{ eV}$ .

### B. Interpretation of the loss features

The comparison between the above theoretical considerations and the loss spectrum at the saturation coverage helps to interpret many of the experimental structures. We first consider the  $I_{V_2}$  loss. As it is clearly seen in Fig. 3, this loss changes in intensity as a function of the H coverage and becomes more structured at saturation coverage. The spectra seem to be consistent with the presence of a H-induced absorption feature at  $\sim 6.5 \text{ eV}$  superimposed on the bulk contribution. The occurrence of two nearby interband transitions (transverse modes), one at the surface and the other in the bulk, should result in three longitudinal modes, as it is actually found in the spectrum at higher coverages (see the arrows in Fig. 3). To illustrate this effect we give in Fig. 6 the results for an ideal case, where the interface loss function [Eq. (1)] has been calculated along the lines of Ref. 8, using analytical dielectric functions based on the Lorentz model for the bulk and for the surface layer. It is seen that when the thickness of the surface layer is about  $3 \text{ \AA}$ , three longitudinal interface losses appear, which are to be associated with two transverse excitations only.

The loss at  $8.4 \text{ eV}$  occurs at almost the same energy as the expected transverse mode (Fig. 5). Since any reminiscence of the  $I_{S_1}$  loss, typical of the GaAs(110) surface, should disappear at monolayer coverage, we interpret this feature as typical of the GaAs(110):H surface. No splitting due to the above-mentioned boundary-condition ef-

fects is observed in this case, probably because of the nature of the energy levels involved in this transverse excitation. The initial states ( $H_4$  bands) are in fact well defined surface states having a strongly localized character (Fig. 5). Therefore its contribution to the surface dielectric function could show a different oscillator strength with respect to the other transverse excitations occurring at the interface. On the other hand, the dielectric properties of the GaAs substrate at  $\sim 8.5$  eV could scarcely affect the interface dielectric function and should give rise to a negligible boundary-condition effect.

The losses at 10.2 and 12.5 eV can be, instead, interpreted within the framework of the above theoretical remarks on the interface dielectric function. The transverse excitation expected at 10 eV on the basis of surface band-structure calculations is, in fact, supposed to give rise to two longitudinal losses due to the vacuum-GaAs(110):H and GaAs(110):H-GaAs(110) boundaries.

The energy localization of the longitudinal losses associated with the transverse excitation starting from the  $H_1$  band ( $\hbar\omega_r \simeq 15$  eV) is less clear. It is likely hidden under the bulk plasmon at  $\hbar\omega_p = 16$  eV.

The "core" losses at 19.9, 20.9, and 22.8 eV of the GaAs(110):H surface are due to the excitation of the Ga 3d core level. In particular, the 19.9-eV loss (labeled by  $I_{S_4}$  in Fig. 3) is the already observed<sup>4,18</sup> Ga 3d surface exciton of the clean GaAs(110) surface.

Figures 2 and 3 show clearly the strong effect of chemisorbed hydrogens on the exciton which disappears completely when the "relative" change of GaAs(110):H work function is  $\Delta\phi = -0.4$  eV. Its sensitivity to hydrogen coverage is confirmed by spectroscopic results obtained by partial yield spectroscopy.<sup>6</sup> The line shape and the energy position of the surface exciton are not affected at all by

hydrogen exposures. This confirms the hypothesis that it is a localized, Frenkel-type, exciton.<sup>19</sup>

## V. CONCLUSIONS

We have been able to single out from the loss spectra of the GaAs(110):H system, electronic excitations characteristic of atomic H chemisorbed on GaAs(110) surface. Based on this analysis we can draw some conclusions about the chemisorption bond in this system.

First of all, we notice that the occurrence of transitions which are associated both with Ga and with As states bound to hydrogen indicates that chemisorption takes place on both surface sites, in agreement with the results of high-resolution vibrational spectroscopy.

Second, the data can be understood by a model with hydrogen atoms linked to the substrate through covalent directional bonds and assuming an unrelaxed substrate. Attempts to assign the main structures on the basis of theoretical calculations for the relaxed substrate do not show a similar agreement with the experiment.

More spectroscopic data are needed to confirm the present analysis and to draw definite conclusions on the geometrical structure of the substrate atoms. Photoemission studies on this subject are, however, in progress.

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