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To cite this version:
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(Reçu le 21 octobre 1986, accepté le 15 décembre 1986)

Abstract. — The interaction of hydrogen ions H$^+$ with the (110) surface of GaAs prepared by cleavage under ultrahigh vacuum has been studied by photoemission yield spectroscopy and controlled by Auger electron spectroscopy and low energy electron diffraction. The ions, having a kinetic energy lower than 100 eV, were produced by an excitation cell connected to the working chamber by a hole 0.5 mm in diameter and could be deflected onto the sample surface. The interaction of H$^+$ with GaAs(110) at progressively increasing doses begins with the two successive stages which have been characterized from the interaction of atomic hydrogen with the same substrate: first an adsorption stage during which hydrogen binds covalently to both Ga and As, then a decomposition stage with formation of Ga metal and, most likely, arsine AsH$_3$ which remains adsorbed on the surface. As the dose of hydrogen ions keeps on increasing, a layer by layer etching of the surface is observed with removal of the hydrogenated compound.

1. Introduction.

Many semiconductor surface treatments involve plasma techniques with hydrogen or hydrogen-containing molecules. In particular, hydrogen plasmas have been shown to be efficient in etching a GaAs(100) surface [1, 2] or cleaning it [3]. The exact composition of a plasma results from many possible reactions [4, 5] and depends on the experimental conditions. It is not usually well known. It appeared of interest to examine separately the interaction of likely components of hydrogen plasmas, namely atomic and ionized hydrogen, with cleaved GaAs(110). This face was chosen because of its fundamental interest and also because it is well known as far as its structural [6] and electronic [7] properties are concerned. The results about the GaAs(110) + H system are reported on in detail elsewhere [8]. Here we focus on the ionized hydrogen interaction, studied by photoemission yield spectroscopy, and compare it with that of atomic hydrogen.

2. Experimental details.

The ultrahigh vacuum (UHV) system used in the present study has been described previously [9]. It is equipped for cleavage, low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and photoemission yield spectroscopy (PYS). On one of the ports was mounted either a tungsten filament, used to produce atomic hydrogen by thermal excitation of molecular hydrogen, or an excitation cell, used as a source for hydrogen ions. In our set-up, the direct particle beam impinges at about 45° from the sample surface.
The ions were produced in an ionization-gauge like excitation cell connected (i) to research grade hydrogen through a bakeable leak valve, and (ii) to the main chamber via a hole 0.5 mm in diameter. This enabled to maintain a total pressure of about $10^{-6}$ torr in the main chamber during exposure after which a pressure in the $10^{-9}$ torr range was recovered rapidly by evacuating the satellite chamber with the UHV system pumping unit through a by-pass. The ions entering the main chamber had an energy of about 80 eV. The direct ion beam travelling in a field-free space had a diameter of about 3.3 mm at the sample position and an average current density of about 50 nA/cm$^2$ giving a flux of $3.7 \times 10^{11}$ singly-charged ions per cm$^2$ and per second. The ions could be deflected onto the sample surface which had been displaced vertically away from the excitation cell axis. This was done to minimize the effect of atomic hydrogen under the assumption that the size of the direct ion beam is also representative of that of the H beam effusing from the excitation cell.

The ions which can possibly be present in an hydrogen plasma are $H^+$, $H_2^+$ and $H_3^+$. $H^+$ appears to be the dominating species in electrodeless discharge systems [4] and in powerful positive ion sources [5]. However our working conditions are much different. They are closer to those of an ionization gauge or a gas analyser. For this reason, we have assumed that the main ionic species present in our system is $H_2^+$ as observed with a quadrupole mass analyser in a H$_2$ ambient. Then, from the current which flows through the sample during exposure, and from the duration of that exposure, we can evaluate the amount of hydrogen atoms which have arrived on the surface. We shall refer to this quantity throughout the present paper and express it in monolayer units (1 ML = 8.84 x $10^{14}$ cm$^{-2}$ for GaAs(110)). One should keep in mind it is merely an indication of the hydrogen dose with which the sample has interacted. Besides the uncertainty on the exact nature of the ions, it does not give the number of hydrogen atoms which are on the surface because desorption, as a result of the interaction, may occur as well as adsorption of atomic hydrogen.

The X-ray oriented GaAs sample (n-type with $10^{18}$ carriers cm$^{-3}$), with precut notches, was cleaved at a base pressure of about $5 \times 10^{-10}$ torr. The (110) face, about $4 \times 5$ mm$^2$ in cross-section, was then exposed to hydrogen ions from the deflected beam at progressively increasing doses up to a total cumulated dose of about 10 ML. After cleavage and after each $H_2^+$ interaction, the photoemission yield spectrum of the surface was recorded in the photon energy range from 3.7 to 6.4 eV. AES and LEED were performed occasionally. AES showed that oxygen, carbon and sulphur were present on the surface after 13 ML of hydrogen. But the Auger peak intensities of these elements were only a few percents of the clean substrate Auger peaks.

3. Results.

LEED revealed that the 1 x 1 diffraction pattern was always observable, even after the largest doses (against a high background then). But the relative intensities of the spots among themselves, at a given electron energy, changed from what they were after cleavage. For instance, at 56 eV, only the (01) and (0$ar{1}$) spots remain visible after 13 ML of hydrogen while other spots such as (0$ar{2}$), (11) and (12) which were quite intense also after cleavage have faded away. This evolution of the GaAs(110) LEED pattern upon $H_2^+$ interaction is similar to what has been observed upon heavy hydrogenation with H [8].

3.1 PYS UP TO 1 ML. — Successive photoemission yield spectra $Y(E)$, recorded against photon energy, after cleavage and after interaction with ionized hydrogen at increasing doses from 0.01 to 1 ML, are shown in figure 1 on a semilogarithmic plot. The corresponding effective densities of filled states, $N^*(E)$ [10,11], obtained by differentiating the $Y(E)$ curves with respect to photon energy, are given in figure 2.

![Fig. 1. — Photoemission yield spectra $Y(E)$ plotted against photon energy for n-type GaAs after cleavage and after interaction with ionized hydrogen at various exposures, expressed in monolayer units.](image-url)
First derivative of the photoemission yield spectra with respect to photon energy, called effective density of filled states $N^*(E)$, plotted against photon energy, for the curves of figure 1, after cleavage and after interaction with ionized hydrogen at various exposures.

The work function $\phi$ which gives the Fermi level position with respect to the vacuum level has been determined by fitting the Fermi distribution function at threshold on $N^*(E)$ or $Y(E)$. The determination is accurate to within $\pm 0.03$ eV after cleavage when there is a large enough density of states at the Fermi level $E_F$. Otherwise, with a low and highly variable density of states at $E_F$, the photon energy at threshold gives an upper limit of $\phi$ with a greater uncertainty towards lower values. The evolution of $\phi$ with ionized hydrogen exposure is given in figure 3 for our n-type sample.

The ionization energy $I$ which gives the position of $E_{Vs}$, the valence band edge at the surface, with respect to the vacuum level, has been obtained from the GaAs valence band contribution. After cleavage, the bands are flat and the high energy part of the $Y(E)$ or $N^*(E)$ curves can be fitted with a function of the form $(E - E_{Vs})^{-2}$ or $(E - E_{Vs})^{-3}$, respectively, giving $I = 5.45 \pm 0.05$ eV. After interaction with H$_2^+$, band bending occurs and its effects cannot be neglected with our sample since the Debye length ($L_D = 39$ Å for $n = 10^{18}$ cm$^{-3}$) is not large enough compared to the photoelectron escape depth ($\sim 12$ Å [12]). The bulk contributions have been computed to include band bending in a way similar to that described previously [10]. The $I$ values resulting from the best fits with an assumed band bending consistent with the observed $\phi$ are plotted in figure 3. One notices $I$ decreases progressively from its after cleavage value to 5.25 eV after interaction with 1 ML of ionized hydrogen, i.e., $E_{Vs}$ moves closer to the vacuum level.

The effective density of filled surface states $N_s^*(E)$ induced by the H$_2^+$ interaction is obtained by subtracting the effective density of bulk states $N_b^*(E)$ from the total effective density of states $N^*(E)$. $N_b^*(E)$ is the valence band contribution computed for the determination of $I$. Such differences are shown in figure 4. They are drawn in linear scale at various hydrogen ion exposures with the energy referred to $E_{Vs}$. They reveal the growth of a band of states centred about 0.13 eV below $E_{Vs}$ with a full width at half maximum of about 0.2 eV, and tailing into the gap.

3.2 PYS BEYOND 1 ML. — In figure 5, the successive $Y(E)$ curves obtained after interaction of GaAs(110) with ionized hydrogen are given in semilog plots for exposures ranging from 2 to 10 ML. After 2 ML, a change appears in the yield curve around $h \nu = 5.5$ eV which becomes a dip after 3 ML. At 4 ML, one observes the complete disappearance of the photoemission signal over a photon energy range of 0.4 eV centred at 5.45 eV, while the yield curve is seen to behave normally at lower and higher photon energies. This phenomenon has already been observed in the GaAs(110) + H system [13]. We refer to it as the « black hole » phenomenon in photoemission yield spectroscopy. Beyond 4 ML, the « black hole » decreases with only a dip observable in $Y(E)$ after 5 ML, and disappears.
at 6 ML. If the GaAs surface keeps on interacting with $H_2$, one observes again a dip in the $Y(E)$ curve (at 7 ML), followed by the «black hole» (at 8 ML), then again also the decrease of the phenomenon (at 9 ML) and its disappearance (at 10 ML). Thus, beyond 1 ML, we observe alternately the appearance and the disappearance of the «black hole» phenomenon.

The work function has been determined from the $Y(E)$ curves of figure 5 and the $\phi$ values are plotted in figure 3 as a function of the hydrogen dose. Beyond 1 ML, $\phi$ alternates between two extreme values. The lower one, at 4.30 eV, is obtained when the «black hole» phenomenon (at 4 and 8 ML) or a large enough dip (at 7 and 9 ML) are observed in $Y(E)$. The other value, at 4.5-4.6 eV, is determined when a dip shows up for the first time (at 2 ML) or when the phenomenon has disappeared (at 6 and 10 ML).

The ionization energy has been determined at 6 and 10 ML when there is no dip in the yield curve, assuming the surface is homogeneous and the overlayer thin enough to neglect the decrease of the substrate contribution. The corresponding $I$ values are plotted in figure 3. The above assumptions may not be valid in the other cases and $I$ was not determined then. It appears to have very likely decreased by as much as 0.3 eV or more from its value at cleavage. The effective densities of states have not been determined either beyond 1 ML. In that exposure range, the decrease of $Y$ around $h\nu = 5.5$ eV perturbs greatly the yield curves and the hypotheses underlying the determination of $N^*(E)$ no longer hold when $Y(E)$ has a negative slope.

4. Discussion

We summarize first briefly the main results concerning the GaAs(110) + H system [8]. Atomic hydrogen interacts in two successive stages with cleaved GaAs. The first interaction stage is an adsorption which saturates with two hydrogen atoms per surface unit cell. H binds covalently to both Ga and As inducing a change in surface reconstruction whereby the substrate surface atoms go back towards their ideal bulk-like positions. The adsorption process occurs without change in ionization energy, and, from very low coverages, it induces a pinning of the Fermi level at about midgap on both n- and p-type samples. A band of H-induced surface states, about 0.22 eV wide, is observed to grow at 0.12 eV below $E_v$. The second interaction stage leads to a dissociation of the substrate into Ga metal and an As hydrogenated compound, arsine $AsH_3$ most likely, which remains adsorbed on the surface and induces a decrease of the ionization energy. It is characterized, upon
heavy hydrogenation, by the appearance of the « black hole » phenomenon around $h\nu = 5.5$ eV [13]. The physical process at the origin of this phenomenon is still unknown. However, it appears to be related to an electronic transition of the AsH$_3$ molecule. This peculiar phenomenon disappears upon heating the sample at 350 °C.

The GaAs(110) + H$_2^+$ system shows great similarities with GaAs(110) + H, at least during the interaction with the first few monolayers of ionized hydrogen when the above interaction stages are also observed.

4.1 UP TO 1 ML. — After cleavage, there are no surface states in the gap and the bands are flat within the accuracy of our determinations, the ionization energy and work function being, respectively, 5.45 eV and 4.05 eV for our n-type sample. This is characteristic of a clean relaxed (110) surface of GaAs [7].

The smallest dose of ionized hydrogen ($\sim 0.01$ ML) increases the work function to, at most, 4.85 eV without much change in $I$ (Fig. 3). Thus, a band bending develops in the n-type substrate as a result of acceptor states which have been generated below $E_F$ in the lower half of the gap upon H$_2^+$ interaction. When the hydrogen ion dose increases up to about 1 ML, $I$ decreases by at most 0.2 eV. However, the simultaneous decrease of $\phi$ (Fig. 3) indicates that the band bending remains roughly constant throughout this interaction stage, $E_F$ being pinned, at least, 0.6 eV above $E_{\text{cv}}$. This pinning of the Fermi level in an n-type GaAs sample has been observed with atomic hydrogen during the adsorption stage [8]. However, it is not typical of hydrogen interaction but has been observed with other adsorbates like O$_2$ [14] or a metal [15]. It sets in at very low doses or coverages and has been attributed [15, 16] to an adsorption-induced change in the surface reconstruction: as a result of the surface substrate atoms moving back towards their bulk-like positions, the Ga-derived and As-derived surface states move towards the gap. In particular, the former move down into the gap bringing in the necessary acceptor states.

Aside from this very general behaviour of cleaved GaAs upon adsorption, the two systems GaAs(110) + H$_2^+$ and GaAs(110) + H have in common the following results which are more specific:

(i) both systems show the same qualitative evolution of the diffraction spots relative intensities, at a given electron energy, in LEED;

(ii) both systems reveal a hydrogen-induced surface state band with the same width ($\sim 0.2$ eV) and centred at the same position ($\sim 0.12$ eV) below $E_{\text{cv}}$. Thus it appears very likely that the same type of adsorption occurs during the first interaction stage in both systems. This means that the hydrogen atoms from ionized hydrogen form covalent bonds with the GaAs substrate. We expect this interaction to take place with both Ga and As like in the atomic hydrogen case [17].

However, some differences exist between the two systems. They concern (i) the ionization energy: $I$ decreases by about 0.2 eV with a 1 ML dose of H$_2^+$ whereas it remains constant during the adsorption stage with H; and (ii) the density of hydrogen-induced surface states: the $N_s^*(E)$ peak determined at 1 ML of H$_2^+$ has a much lower intensity, by a factor of about 6, than the surface state band obtained at saturation of the H adsorption stage. A slight oxygen contamination in the H$_2^+$ experiment, and a possible sputtering effect of the ions might be invoked to explain these two differences respectively. The observed discrepancies may, more likely, be the consequence of a greater heterogeneity of the GaAs + H$_2^+$ system arising from a different reactivity of H$_2^+$ as compared to H, with respect to GaAs. H$_2^+$ may be less efficient than H towards adsorption from the mere fact it has to be broken up first. Conversely, it may be more efficient than H towards the next interaction stage leading to the formation of AsH$_2$ radicals or arsine upon interaction with As-H for instance. Thus, with H$_2^+$, the second interaction stage (dissociation) might start much earlier than with H preventing the adsorption stage from reaching saturation. This would explain both the low density of hydrogen-induced surface states and the decrease of $I$ due to the early formation of polar species such as AsH$_3$ molecules, in the case of H$_2^+$. Indeed the adsorption stage is not observed as well with H$_2^+$ as with H. The limit of 1 ML does not mean adsorption saturates at this dose. It has been chosen because, up to it, the $Y(E)$ curve is « normal », i.e., there is no clear evidence that $Y$ has decreased at $h\nu = 5.5$ eV.

4.2 FROM 1 ML TO 4 ML. — The evolution of the yield curves upon H$_2^+$ exposure, from 1 to 4 ML, resembles that observed during the dissociation stage upon H interaction. In particular, the « black hole » which appears at 4 ML is quite similar to that obtained with H. It is only more intense, the photoemission signal being zero over a 0.4 eV range, against a range of about 0.2 eV with H. The « black hole » phenomenon is the signature of the particular compounds which are responsible for it. The chemical species which have formed then on the surface must be the same in both systems, namely Ga metal and, most likely, adsorbed arsine. In the H$_2^+$ system at 4 ML, not only the « black hole » is larger than with H, but the threshold is truly metallic with a work function at 4.30 eV corresponding to that of Ga metal [18]. This observation is quite consistent with the dissociation scheme.
4.3 BEYOND 4 ML. — We have just seen that, up to 4 ML, cleaved GaAs interacts with H\textsubscript{2} through the same stages as observed with H: an adsorption, then a dissociation of the substrate. However, the two systems differ at larger doses. In the case of GaAs + H, if the hydrogen dose is increased beyond 1.6 \times 10^3 Langmuirs (the lowest H\textsubscript{2} dose in the presence of the hot filament at which the « black hole » phenomenon appeared in our set-up), the « black hole » becomes more intense and widens slightly. On the contrary, after a new hydrogen ion exposure beyond 4 ML, this phenomenon decreases in intensity at 5 ML and disappears at 6 ML (Fig. 5). In the latter case, the yield curve has a « normal » behaviour, i.e., it is a continuously increasing function of \( h\nu \). The chemical species at the origin of the « black hole » phenomenon are no longer present on the surface. The H\textsubscript{2}\textsuperscript{+} interaction at this stage has an effect similar to heating the sample in the GaAs + H system (we have checked with another cleavage that annealing GaAs + H\textsubscript{2} when the « black hole » was present in \( Y(E) \) had the same consequence of eliminating it). Thus the H\textsubscript{2}\textsuperscript{+} impact as well as heating induce the desorption of the hydrogenated species which leave the surface as stable gaseous molecules, AsH\textsubscript{3} most likely. Either the kinetic energy of the ions is sufficient to break the bond between AsH\textsubscript{3} and the substrate, or the H\textsubscript{2}\textsuperscript{+} ions interact with AsH\textsubscript{2} radicals, for instance, to form AsH\textsubscript{3} which goes off. Ga remains on the surface where it clusters into droplets. The change from a relatively spread out Ga metal when the « black hole » exists, to droplets of Ga when the phenomenon has disappeared is consistent with the threshold evolution of the yield curves. From 4 ML to 6 ML of hydrogen ions (Fig. 5), the threshold shifts from a true metallic character with the work function of Ga metal at 4.30 eV, to a less steep increase at higher energies. The apparent increase of \( \phi \) once Ga has clustered into droplets results from a smaller portion of the surface being covered by the metal.

At 6 ML, next to the Ga droplets, the surface is essentially GaAs with some adsorbed hydrogen. Then, the whole process can start over again upon H\textsubscript{2}\textsuperscript{+} interaction, namely, appearance of the « black hole » phenomenon (at 8 ML) followed by its disappearance (at 10 ML) corresponding, respectively, to the formation of an arsine layer upon dissociation of the substrate, followed by its desorption. Thus we observe a cycling of the chemical species present on the GaAs surface. It is indicative of a layer by layer etching of the substrate without deep perturbation since the LEED pattern is still observable.

As can be seen on the \( Y(E) \) curves of figure 5, a progressive deterioration of the « black hole » takes place. At 8 ML, the phenomenon is not as intense as at 4 ML: (i) although the work function is that of Ga metal, the threshold is not as steep; (ii) the photon energy range over which the photoemission signal is zero, is not as large. It indicates, very probably, an alteration of the quality of the surface due to a greater disorder induced both by the H\textsubscript{2}\textsuperscript{+} ions and by possible impurities (the 8 ML curve was recorded more than two days after cleavage). As a result, a greater inhomogeneity exists on the surface modifying locally the adsorption-desorption kinetics.

5. Conclusion.

In this paper, we have shown there is a great similarity between ionized hydrogen, H\textsubscript{2}\textsuperscript{+}, and atomic hydrogen in their interaction with cleaved GaAs. It appears both in the adsorption stage when the same covalent bonds are formed with the substrate, and in the dissociation stage leading to the same decomposition products. With the ions, another interaction stage has been observed leading to the desorption of arsine and a metal enrichment of the surface. The recurrence of these interaction stages induces a layer by layer etching of the semiconductor surface. This process has not been observed with atomic hydrogen. It means that the removal of the As-hydrogenated compound which has formed on the surface is not the mere consequence of a chemical reaction with hydrogen. It results, most likely, from the impact of the ions because of their kinetic energy. In this process, very little damage is done to the substrate beyond the first surface layer since the LEED diagram is still visible after the largest hydrogen ion dose. The effect of ion impact exists throughout the interaction with GaAs. It is partly responsible for the heterogeneity which has been pointed out at the beginning of the interaction with ionized hydrogen and during the progressive deterioration of the system at higher hydrogen ion doses. This means that to avoid any damage upon ion impact, H\textsubscript{2}\textsuperscript{+} ions of lower energy would have to be used, and heavier ions would require a lower energy still. Considering the ions we have used had a mass of 2 and a kinetic energy of about 80 eV, an equivalent energy with respect to damage for ions from heavier elements would fall very quickly below 10-20 eV.
References