

## Hydrogen Adsorption on GaAs(110) Studied by Electron-Energy-Loss Spectroscopy

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By means of high-resolution electron-energy-loss spectroscopy (resolution  $\sim 7$  meV) atomic H and D are shown to adsorb on GaAs(110) on Ga and on As sites. From a comparison of the H and D vibration frequencies Morse adsorption potential curves for hydrogen on Ga and on As sites are constructed. The results are compared with thermal desorption data.

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Thermodynamical data of an adsorption system are usually derived from thermal desorption spectroscopy and related techniques. In this paper we show for the first time how vibrational frequencies of an adsorbate can be used to derive dissociation energies for the adsorbate/substrate chemical bond and how a complete potential-versus-distance curve can be constructed from the vibrational data. We have studied the vibrational spectra of atomic hydrogen (H) and deuterium (D) adsorbed on GaAs(110) surfaces. This adsorption system is of considerable interest for a number of surface reactions that are important in the technology of III-V compound devices. From the present results it is obvious that hydrogen is chemisorbed both on Ga and on As sites. By comparing the H and the D frequencies the anharmonic part of the chemisorption potential on both sites is derived. The anharmonicity is related to the dissociation energy and therefore conclusions about the chemisorption bond strength are possible.

The samples were prepared from single-crystal bars of  $n$ -type material (Te doped;  $n = 4 \times 10^{17}$   $\text{cm}^{-3}$  and  $\mu = 3000$   $\text{cm}^2/\text{V s}$ ) and of semi-insulating GaAs which is highly doped with Cr ( $p$  type) causing specific resistivities above  $10^6$   $\Omega$  cm at 300 K. For cleavage in ultrahigh vacuum (UHV,  $p < 10^{-8}$  Pa) the double wedge technique was used. Gold-bonded contacts on the rear side of the  $n$ -type samples allowed direct electrical heating. Since molecular hydrogen does not adsorb at 300 K,  $\text{H}_2$  and  $\text{D}_2$  had to be dissociated by a hot tungsten filament and/or by running ion pumps during gas inlet. The exact H and D doses therefore are not known. The production of atomic H and D was monitored by measuring the increase of the surface conductivity of a preannealed ZnO crystal. The presented loss spectra were recorded in the direction of the specular beam with an angle of

incidence of  $70^\circ$  and a primary electron energy of 5 eV. The used single-stage spectrometer (resolution: 7 meV at  $3 \times 10^{-11}$  A current at multiplier, without sample) is of the  $127^\circ$  deflector type described previously.<sup>1</sup>

After cleavage in UHV the energy-loss spectra measured on semi-insulating GaAs(110) exhibit a series of equidistant energy losses and gains which are due to scattering on Fuchs-Kliwer surface phonons (Fig. 1).<sup>2</sup> On  $n$ -type material with carrier concentrations in the  $10^{17}$   $\text{cm}^{-3}$  range additional structures due to surface plasmons are observed.<sup>3</sup>

During hydrogen adsorption the surface phonon losses up to about  $1200$   $\text{cm}^{-1}$  are not significantly changed; only the intensity decreases by a factor of  $\sim 10$ . Two characteristic hydrogen peaks appear at  $1890 \pm 5$   $\text{cm}^{-1}$  and  $2150 \pm 10$   $\text{cm}^{-1}$  (Fig. 1, curve in full line). Adsorbed D in comparable coverage gives rise to losses at  $1380 \pm 10$   $\text{cm}^{-1}$  and  $1660 \pm 20$   $\text{cm}^{-1}$  (Fig. 1, curve in broken line). The errors in the spectral positions of these bands are mainly due to uncertainties in the background. The maximum errors are evaluated by analyzing spectra from different runs with different amplification factors and by taking into account different background intensities. In the low-energy range below  $1000$   $\text{cm}^{-1}$  no vibrational losses due to H or D could be detected because of the prominent phonon losses. In spite of careful investigation no loss is found in the wavenumber range near  $4400$   $\text{cm}^{-1}$ , where the stretching vibration of  $\text{H}_2$  is expected.<sup>4</sup> As far as the two losses at  $1890$  and  $2150$   $\text{cm}^{-1}$  are concerned, the results on  $n$ -type samples coincide with those on semi-insulating material. This observation rules out an interpretation of the  $2150$ - $\text{cm}^{-1}$  loss in terms of a combination of the  $1890$ - $\text{cm}^{-1}$  loss with a surface phonon; the phonon cross section on  $n$ -type samples is considerably smaller than

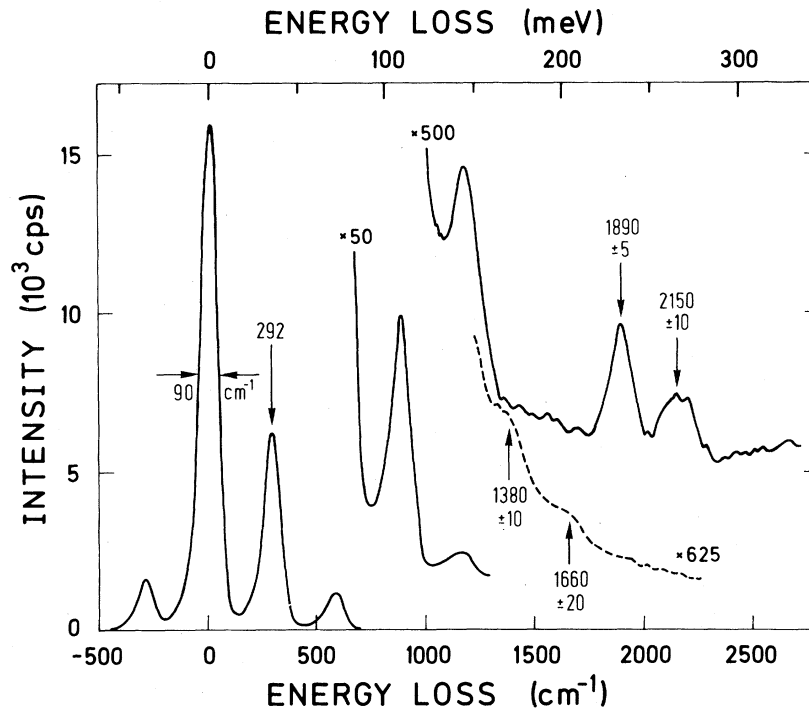


FIG. 1. Loss spectra measured on two different cleaved (110) surfaces after adsorption of H (full line) and D (broken line). Quantum energy of Fuchs-Kliewer surface phonons:  $292 \text{ cm}^{-1}$ .  $\text{H}_2$ ,  $\text{D}_2$  exposures: 1000 L (H and D doses unknown;  $1 \text{ L} = 10^{-6} \text{ Torr sec}$ ).

on semi-insulating GaAs.<sup>3</sup>

In a further series of experiments the thermal desorption of chemisorbed H was studied by recording the integrated intensity of the two characteristic peaks at  $1890$  and  $2150 \text{ cm}^{-1}$  in dependence on annealing temperature. After saturation with adsorbed H, the surface was annealed step by step, each time for 5 min, and loss spectra were recorded after cooling down to room temperature. The decrease of the peak intensities is shown in Fig. 2. The relatively large spread of the data for the first annealing cycles seems to be due to instabilities of the electron optics after gas inlet (work function of the apertures, etc.).

The interpretation of the two vibrational bands becomes evident from a comparison with molecular vibrations: The symmetric/antisymmetric As-H (As-D) stretching vibrations in  $\text{AsH}_3$  ( $\text{AsD}_3$ ) are found at  $2116 \text{ cm}^{-1}/2123 \text{ cm}^{-1}$  ( $1523 \text{ cm}^{-1}/1529 \text{ cm}^{-1}$ ).<sup>5</sup> The corresponding Ga-H (Ga-D) vibrations in trimethylamine-halogenogallanes [ $(\text{CH}_3)_3\text{N}(\text{GaH}_{3-x}\text{Cl}_x)$ ;  $x = 0, 1, 2$ ] are between  $1819 \text{ cm}^{-1}/1835 \text{ cm}^{-1}$  ( $1324 \text{ cm}^{-1}$ ) for  $x = 0$  and  $1949 \text{ cm}^{-1}/1968 \text{ cm}^{-1}$  ( $1393 \text{ cm}^{-1}/1408 \text{ cm}^{-1}$ ) for  $x = 2$ .<sup>6</sup> Atomic H and D is therefore adsorbed both on Ga

and on As surface sites. Both sites are found in equal number on the nonpolar (110) surface. Based on the assumption that for saturated adsorption all Ga and As surface atoms bond an H atom (monolayer coverage) the inelastic scattering cross section according to Evans and Mills<sup>7</sup> determines the absolute value of the effective

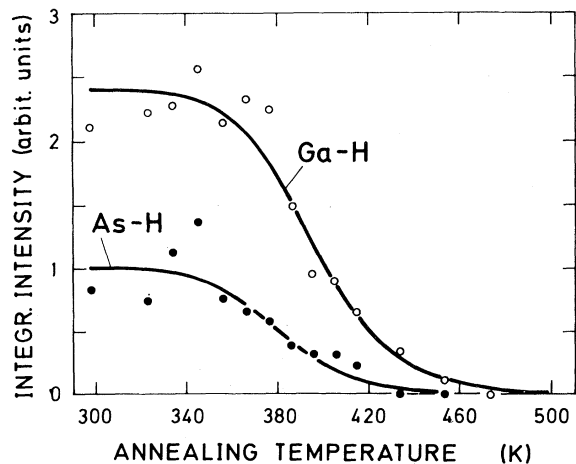


FIG. 2. Integrated intensity of the two H losses at  $1890 \text{ cm}^{-1}$  (Ga-H) and  $2150 \text{ cm}^{-1}$  (As-H) vs annealing temperature.

dynamic ionic charge  $e^*$  of the adsorbed H atoms. The experimental intensity ratios  $I_{\text{H-Ga}}/I_0$  and  $I_{\text{H-As}}/I_0$  of the Ga-H and the As-H peaks with respect to the integrated primary intensity  $I_0$  yield effective charges  $e_{\text{H-As}}^* = 0.038e$  and  $e_{\text{H-Ga}}^* = 0.042e$  ( $e$  is the elementary charge). In spite of the smallness of  $e^*$  the net effect of H adsorption is the formation of a depletion layer.<sup>3</sup>

According to their mass difference the frequencies of the H and D vibrations should be related by  $\sqrt{2}$ , if the vibrational potential is harmonic and if the Ga and As bonding partners have an infinite mass. The effect of a finite mass can be estimated from the reduced mass ratios of the molecules As-H to As-D and Ga-H to Ga-D. A maximum deviation from  $\sqrt{2}$  of only 0.7% is obtained. Furthermore, since the surface phonon frequencies are an order of magnitude lower than the H and D frequencies,<sup>2</sup> the GaAs surface itself is assumed to be solid in the present context. The H and D frequencies on the As and on the Ga site, however, are related by factors 1.37 and 1.30 (Fig. 1), which are significantly different from  $\sqrt{2}$ . This can be explained by the anharmonicity and the finite dissociation energy  $E_D$  of the vibrational potentials. Because of their chemical identity the potentials for H and D are equal. Only the H atoms are lighter and therefore more highly excited than the D ones. Their first excited vibrational level is significantly shifted

down (compared with a purely harmonic potential) because the finite dissociation energy is related to the anharmonicity. From this shift  $E_D$  can be calculated. With a Morse potential<sup>4,8</sup> (Fig. 3, inset), which is well known as a good approximation in diatomic molecules, the vibrational wave equation is solved rigorously giving the following vibrational-energy levels  $E_n$  (Ref. 8):

$$E_n = \hbar\omega_0(n + \frac{1}{2}) - \hbar\omega_0 x_0(n + \frac{1}{2})^2 \\ = (2E_D \hbar^2 \beta^2 / \mu)^{1/2} (n + \frac{1}{2}) - \frac{1}{2} (\hbar^2 \beta^2 / \mu) (n + \frac{1}{2})^2, \quad (1)$$

where  $\mu$  is the reduced mass, in the present case of a solid surface, the mass of D and H, respectively.

From the experimentally determined excitation energies  $\hbar\omega_{\text{H-As}} = E_1(\text{H-As}) - E_0(\text{H-As})$ ,  $\hbar\omega_{\text{D-As}} = E_1(\text{D-As}) - E_0(\text{D-As})$ , and the corresponding values for the Ga site  $\hbar\omega_{\text{H-Ga}}$ ,  $\hbar\omega_{\text{D-Ga}}$  the two parameters  $E_D$  and  $\beta$  are calculated for both adsorption sites. From  $\beta$  the anharmonicity terms  $\hbar\omega_0 x_0$  [Eq. (1)] for the corresponding chemisorption bonds are also obtained. In wave numbers they are 105  $\text{cm}^{-1}$  for the Ga-H bond, 52  $\text{cm}^{-1}$  for the Ga-D, 338  $\text{cm}^{-1}$  for the As-H, and 169  $\text{cm}^{-1}$  for the As-D. The order of magnitude is the same as for some two-atomic molecules<sup>4</sup>: HCl, 52  $\text{cm}^{-1}$ ; HF, 90  $\text{cm}^{-1}$ ; OH, 83  $\text{cm}^{-1}$ . The dissociation energy on the Ga site  $E_D(\text{Ga})$  is derived as  $1.3 \pm 0.3$  eV; that on the As site emerges as  $0.73 \pm 0.1$  eV. The corresponding Morse potentials are plotted in Fig. 3.

Typical bonding energies for As-H bonds in free molecules are considerably larger, i.e., in the order of 2.5 eV. On the other hand, the magnitude of about 1 eV complies with other hydrogen adsorption systems.<sup>9</sup> Assuming that the repulsive part of the potential (steep slopes at  $r < r_0$ ) essentially determines the equilibrium bond length  $r_0$ , one might conclude that the bond length for the Ga-H bond is about 0.15 Å larger than that for the As-H bond. The same tendency follows from a comparison of the covalent bonding radii of Ga (1.26 Å) and As (1.15 Å).

The difference in dissociation energy for H on Ga and on As sites is contrasted by a similar desorption temperature for both sites (Fig. 2). Desorption, however, is molecular:  $\text{H}_2$  molecules rather than atomic H are detected in thermal desorption.<sup>10</sup> Furthermore,  $\text{H}_2$  molecules do not adsorb at 300 K; they have to be predissociated. Desorption of  $\text{H}_2$  might therefore be explained by at least two different processes taking into account adatom-adatom interaction. First, two H

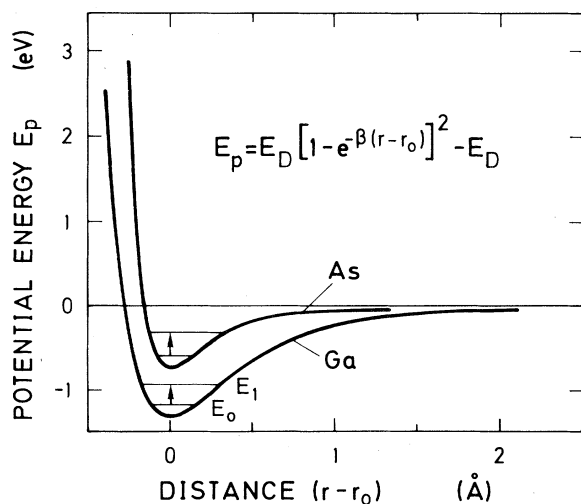


FIG. 3. Morse potentials  $E_p(r-r_0)$  for hydrogen adsorbed on As and on Ga sites.  $E_D$  is the dissociation energy. The first two H-vibrational levels  $E_0$  and  $E_1$  and the experimentally observed transitions (arrows) are also plotted. The potentials are referred to the same equilibrium position  $r_0$ .

adatoms could recombine with subsequent molecular desorption; second, atomic H could desorb from one site with concurrent H transfer from a neighboring site to the empty one, followed by recombination of the two desorbing H atoms. Both processes might involve different sites (a Ga and an As site) or equal sites (two Ga or two As sites). Desorption from different sites would lead to a single rate-limiting step for the whole desorption process, and the average Ga/As site coverage ratio would be the same at any coverage. If the desorbed H<sub>2</sub> species originates from equal sites, two more or less independent desorption processes with two desorption energies result. The barriers from the two sites, however, might be much more similar than the H atom potential wells in Fig. 3 indicate, because the desorption kinetics is determined by a superposition of these "atomic potentials" and a "molecular potential" describing essentially the repulsive interaction, when an H<sub>2</sub> molecule is approaching the surface from large  $r - r_0$  values. For large distances this "molecular potential" approaches the limit  $-4.74$  eV (dissociation energy of H<sub>2</sub> on the scale of Fig. 3). From the present results no decision between the desorption mechanisms discussed is possible.

Without knowledge of further details the curves in full line in Fig. 2 are fitted to the experimental data under the assumption of second-order desorption kinetics. With an assumed desorption energy for the As site of 0.7 eV/atom a preexponential factor  $k_2 = 2 \times 10^{-7}$  cm<sup>2</sup>/s fits best. For

the Ga site this  $k_2$  yields a desorption energy of 0.73 eV/atom. The relatively small  $k_2$  as compared with H on metal surfaces<sup>9</sup> may be related to a low surface mobility of the adsorbed H and/or steric hinderances upon desorption.

Future investigations on the present adsorption system may be concentrated on details of the desorption mechanism and on probable reconstruction changes during H adsorption and desorption.

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