Dynamics of Hydrogen Adsorption on GaAs Electrodes

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(Received 4 December 1997)

In situ infrared spectroscopy unravels the dynamics of hydrogen adsorption on GaAs(100) electrodes. Hydrogen cathodically adsorbs at arsenic sites only and replaces As-OH groups present in the anodic range, causing change in the surface dipole potential. The absolute submonolayer coverages depend on potential and result from a competition between cathodic hydrogenation and anodic or chemical hydroxylation. Surface As-H is identified as the intermediate in hydrogen gas evolution. Its electrochemical reduction is the rate-limiting step of the reaction. [S0031-9007(98)06102-X]

Hydrogen adsorbed at the surface of solids plays an important role in different fields of surface and materials science. It diffuses into the materials, causing embrittlement and, in the case of semiconductors, lowering conductivity by orders of magnitude [1]. It affects surface electrical properties, for instance leading to record low surface recombination rates of photocarriers at silicon surfaces [2]. At the surface of heterogeneous catalysts, it is a reaction intermediate in various commercially important reactions. Here, we examine its role in the cathodic production of hydrogen gas, a promising fuel for the chemical storage of energy. In this reaction, two electrons are transferred from a metal or semiconductor electrode to two aqueously solvated protons $H^+(aq)$, yielding a hydrogen gas molecule $H_2(g)$; a hydrogen atom is temporarily adsorbed after transfer of the first electron. The fraction of the surface covered by adsorbed hydrogen is determined kinetically, by the relative rates of adsorption and desorption. With n-type gallium arsenide, we present the first quantitative determination of the hydrogen surface coverage of an electrode and the first dynamic study of hydrogen adsorption by *in situ* infrared spectroscopy in real time.

The *in situ* spectroscopic detection of hydrogen adsorbed at electrode surfaces is based on the resonant vibrational absorption of hydrogen-to-surface bonds. Despite considerable experimental difficulties, a few authors reported infrared absorption by hydrogen adsorbed on platinum cathodes, although some controversy exists concerning peak assignments [3]. Surface hydrogen is more conveniently detected at attenuated-total-internal-reflection prisms of semiconducting electrodes such as GaAs [4], and this will be done here. Until now, little was known about hydrogen adsorption on GaAs electrodes, although it was found that formation of an H_2 molecule requires two conduction band electrons and that some transient photocurrents could probably be ascribed to oxidation of surface hydrogen [5].

The experiments were performed on Si-doped ⟨100⟩-oriented n-GaAs single crystals grown by the liquid Czochralski method from MCP Wafer Technology, U.K. ($N_d = 8 \times 10^{15}$ cm^{-3}) and from the Institute of Elec-

tronic Materials Technology, Poland ($N_d = 4 \times 10^{15}$ and 7×10^{16} cm^{-3}). The surface was pretreated according to a standard recipe [6]. The electrochemical cell is described in Ref. [7], with the vertically oriented prismatic GaAs electrode (45° angles) exposing an area of 1 cm^2 to a circulating aqueous solution of HCl or NaOH. It includes a platinum counter electrode and an Ag/AgCl in saturated KCl reference electrode. When needed, illumination was achieved using a white light source. Infrared absorbance was measured with a Bomem MB 100 Fourier-transform infrared spectrometer. The absorbance at wave number σ is defined as $(1/N)\ln[I^\sigma(U_0)/I^\sigma(U)]$, where $N \approx 10$ is the number of useful reflections at the electrochemical interface, $I^\sigma(U)$ the light intensity at wave number σ reaching the detector at potential U, and $I^\sigma(U_0)$ the same but under reference conditions at potential U_0. Changes in flatband potential were determined by interrupting the cyclic potential scans every 100 ms for a 1 ms period at various positive potentials, at which the capacitance of the semiconductor space charge layer was measured (for details, see Ref. [8]). The experiments were carried out at room temperature on a short time scale, so that in-diffusion of hydrogen can be neglected.

Figure 1 shows the change in interfacial infrared absorbance as a result of going from the potential where
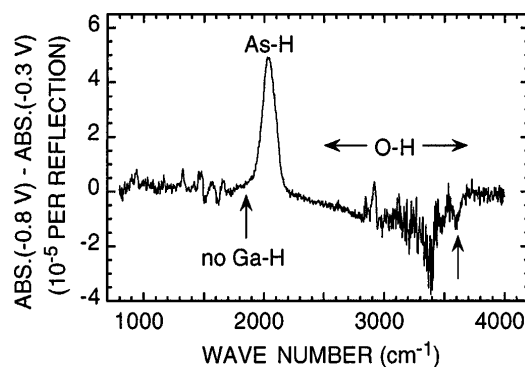

FIG. 1. Change in infrared absorbance of the n-GaAs/6 M HCl interface when the applied potential is changed from -0.3 to -0.8 V vs Ag/AgCl (1500 cycles of 12 s).

no current is measured in the steady state (-0.3 V vs Ag/AgCl) to a potential where hydrogen evolution occurs (-0.8 V vs Ag/AgCl). Absorbance increases at 2050 cm^{-1} and decreases in the 2500–3700 cm^{-1} range. Comparison with the literature indicates that the absorbance at 2050 cm^{-1} corresponds to As-H bonds only; in contrast, spectra of hydrogen adsorbed on GaAs(100) from the gas phase show absorption both by As-H and Ga-H [9]. We ascribe the absorbance decrease in the 2500–3700 cm^{-1} range to loss of surface OH-groups, present at the surface in the anodic range and replaced by adsorbed hydrogen in the cathodic range. The signal might arise either from surface OH-groups or from H$_2$O molecules; however, changes in water absorption would have occurred over a narrower range (from 3000 to 3500 cm^{-1}), and additional changes would have been seen at 1650 cm^{-1} (H-O-H bending modes). Furthermore, the separate peak at 3600 cm^{-1} evokes absorption by isolated OH-groups not hydrogen bonded to other OH-groups, which leads to the ascription of the broad signal to AsO-H. Absorption by As-O bonds falls outside our spectral window. Peak assignments were verified by measurements in deuterated solutions, in which the signals shift to wave numbers lower by a factor $\approx \sqrt{2}$, due to the higher reduced mass of the oscillators [4]. The As-H bonds were found to absorb p-polarized light more strongly than s-polarized light [4], confirming that they are at the surface rather than inside the solid.

Similar switching from a OH- to a H-terminated surface was inferred from current-potential curves on germanium [10] and recently confirmed by in $situ$ infrared spectroscopy [11]. Our results explain why, in contrast to GaAs under vacuum conditions [9], GaAs(100) surfaces can be found unreconstructed at the solution interface, as shown by atomically resolved in $situ$ atomic force microscopy [12]: before hydrogen is adsorbed, dangling bonds are already saturated with adsorbed OH-groups. Here, the surface is not ideally flat but microrough, due to chemical oxidation by dissolved oxygen, anodic dissolution by holes, and cathodic decomposition. We demonstrated elsewhere that a minor percentage of the cathodic current is due to decomposition reactions which cause surface roughening [4].

Since adsorption and desorption compete continuously at every surface site, it is crucial to examine the reaction pathway. The first step in the mechanism of hydrogen gas evolution at a cathode is the reduction of a solvated proton, yielding an adsorbed hydrogen atom H$_{ads}$,

$$H^+(aq) + e^- \rightarrow H_{ads}. \qquad (1)$$

For a given electrode, an important question is whether the second step proceeds by surface diffusion to another adsorbed hydrogen atom (2a) or by a second charge transfer step at the same site (2b) [13]:

$$H_{ads} + H_{ads} \rightarrow H_2(g), \qquad (2a)$$

$$H_{ads} + H^+(aq) + e^- \rightarrow H_2(g). \qquad (2b)$$
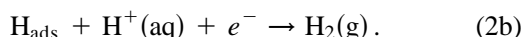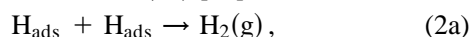
Results of time-resolved measurements illustrated in Fig. 2 show that in the dark at positive potentials, the disappearance of As-H is due only to anodic reaction with holes (negligible here, the current density j was ≈ 20 nA cm^{-2}) and chemical reaction with dissolved oxidants (e.g., oxygen). This is direct evidence against there being mobile adsorbed hydrogen atoms which combine to form hydrogen molecules, reaction (2a). The negligible mobility of adsorbed hydrogen is in line with the covalent character of the As-H bond. Therefore, in the cathodic range, a hydrogen molecule is produced by two consecutive electron transfer steps at the same site, reactions (1) and (2b).

In subsequent measurements, the oxygen concentration was kept minimal by purging the solution using a flow of purified nitrogen and by using a salt bridge to isolate the counter electrode, at which oxygen is produced during the cathodic polarization of GaAs.

Electrochemistry presents an opportunity absent in the case of hydrogen adsorption from the gas phase: The possibility to determine absolute hydrogen surface coverages by coulometric titration. After measurement of the As-H absorbance under cathodic conditions, the potential is changed to the steady-state potential under illumination. Just after the jump, a photocurrent appears and decreases to zero as surface hydrogen is removed (see Fig. 3). The anodic charge measured by integrating the transient photocurrent is proportional to the initial As-H absorbance (Fig. 4). In HCl solutions, polarization must be kept brief at potentials $U < -0.8$ V, in order to limit the formation of metallic gallium [4]. The proportionality is strong evidence that the anodic charge is used almost exclusively for the oxidation of surface hydrogen. The same proportionality constant is found in acidic and alkaline solutions with different GaAs samples and light intensities. On the assumption, suggested by Fig. 1, that all As-H is oxidized to As-OH, requiring two holes per As-H, integrated absorbances by surface As-H can be converted to absolute surface coverage using Fig. 4. At the most negative potentials, surface hydrogen coverage is of the order of a monolayer, 6.26×10^{14} cm^{-2} arsenic
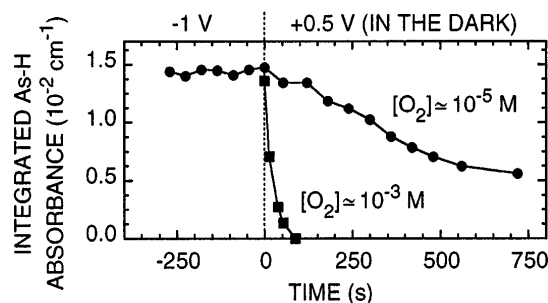

FIG. 2. Disappearance rate of As-H from the n-GaAs surface in 1 M HCl, after stepping potential from -1 V to $+0.5$ V vs Ag/AgCl in the dark, for two different concentrations of dissolved oxygen.
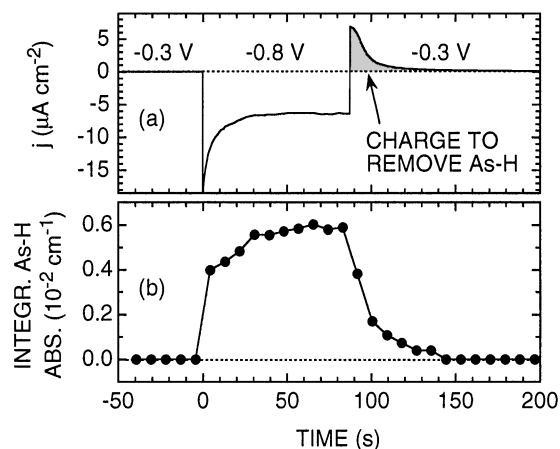
FIG. 3. Changes in (a) current density and (b) As-H absorbance of illuminated n-GaAs electrodes in 1 M HCl upon stepping potential from -0.3 to -0.8 V vs Ag/AgCl and back.

photon under illumination [14]. In the steady state, anodic current causes dissolution of the semiconductor [14], while in the 50 mV s^{-1} scan, as long as As-H is present, all anodic current is consumed for the oxidation of surface hydrogen. The high As-H coverages, including under conditions where cathodic current density is low, demonstrate that step (2b) is rate limiting for hydrogen gas evolution.

One important difference with a Schottky diode is that the applied potential drops partly across the semiconductor space charge layer and partly across the much thinner Helmholtz layer on the electrolyte side of the interface [14]. In Fig. 5(c), changes in potential drop across the Helmholtz layer are revealed by changes in the flatband potential. In the reverse bias range, U_{fb} is -0.84 V in the dark and somewhat more positive under illumination, due to the positive charge of dissolution intermediates [15].

atoms at an unreconstructed GaAs(100) surface. A higher concentration of As-H bonds might suggest the presence of arsenic dihydride, but it is just as likely due to surface (micro)roughness.

The hydrogen surface coverage of illuminated n-GaAs electrodes in 1 M HCl solution was monitored during cyclic potential scans at two different scan rates. Current density is shown in Fig. 5(a), hydrogen surface coverage in Fig. 5(b), and flatband potential U_{fb} in Fig. 5(c). The 0.5 mV s^{-1} scan approximates steady state conditions, while the 50 mV s^{-1} scan illustrates the system dynamics.

The n-GaAs electrochemical interface is a rectifying contact, much like a Schottky diode. Under forward bias, cathodic current density due to hydrogen gas evolution changes exponentially with the applied potential, while hydrogen surface coverage changes more or less linearly. Under reverse bias, the anodic current density is very low in the dark and corresponds to one hole per absorbed
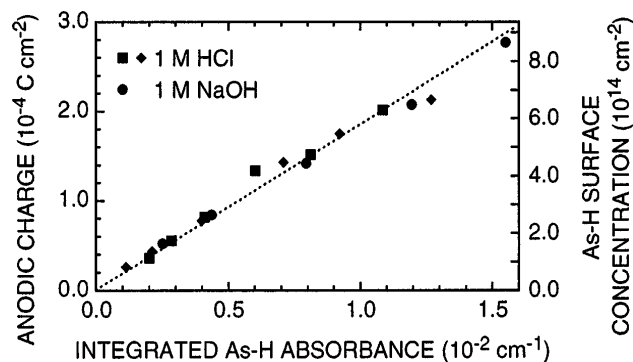

FIG. 4. Anodic charge required to remove hydrogen from n-GaAs surfaces in 1 M HCl or 1 M NaOH as a function of the initial As-H absorbance (different symbols refer to different electrodes).
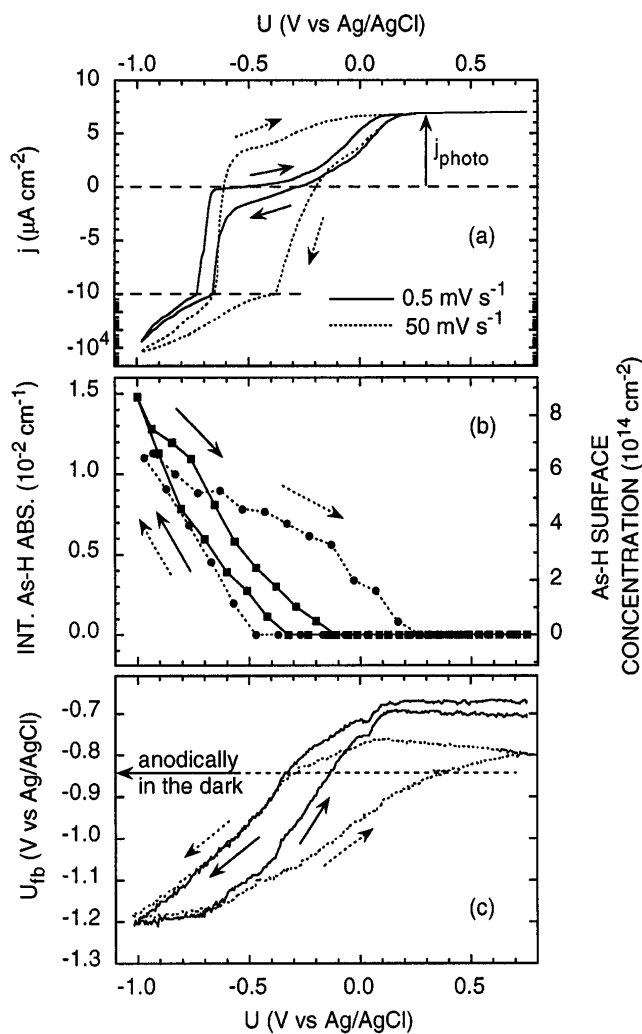

FIG. 5. (a) Current density, (b) surface coverage by hydrogen, and (c) flatband potential of illuminated n-GaAs electrodes in 1 M HCl monitored during cyclic potential scans at two different scan rates (same light intensity as Fig. 3).
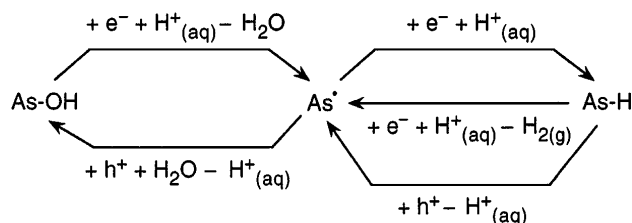
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FIG. 6.   Reaction scheme for changes in surface coverage of GaAs cathodes.

Under forward bias, U_{fb} shifts negatively, in agreement with steady-state measurements by Uhlendorf *et al.* [16]. Our dynamic measurements clearly indicate that the position of U_{fb} is correlated to the hydrogen surface coverage. U_{fb} and hydrogen surface coverage show approximately the same hysteresis, about 200 mV during the 0.5 mV s^{-1} scan and much more during the 50 mV s^{-1} scan. During the negative scans, first the positive surface charge disappears, and then, an additional negative U_{fb} shift of about 50 mV occurs per 10^{14} cm^{-2} As-H bonds. During the positive scans, first As-H disappears, after which positive surface charge reappears, both causing a positive shift of U_{fb}. This is the first direct evidence in electrochemistry that a change from OH- to H-surface coverage causes a change in the surface dipole potential.

It has often been assumed that hydrogen surface coverages of cathodes are determined by the relative rate constants of the two steps of the hydrogen gas evolution reaction [13]. However, our measurements indicate that this picture is not complete for GaAs. Its surface is covered either by H- or OH-groups, so that a reaction capable of producing a surface OH-group must also exist. Moreover, the switch from As-OH to As-H or back requires two charge carriers, implying the presence of a short-lived As$^\bullet$ radical intermediate. Hydroxylation of As$^\bullet$ consumes a hole (or another oxidant) rather than an electron, and this is probably the reason for the hysteresis during fast cyclic potential scans: Whereas hydrogenation of As$^\bullet$ is the rapid step of the dominant reaction—hydrogen gas evolution—hydroxylation is a reaction whose rate is limited by the flux of holes towards the surface. The most important reaction steps are summarized in Fig. 6.

In conclusion, *in situ* infrared spectroscopy unravels, for the first time, the microscopic mechanism of hydrogen gas evolution on GaAs cathodes. Surface hydrogen is bound to arsenic atoms and replaces surface OH-groups present under anodic conditions, causing a change in surface dipole potential. Our coulometric titration allows the quantitative determination of absolute hydrogen surface coverages. Cathodic hydrogenation of As-H is rate limiting for the hydrogen gas evolution reaction, and hydrogen surface coverage results from a competition between cathodic hydrogenation and anodic or chemical hydroxylation. All the observations can be accounted for quantitatively in a detailed kinetic model which will be published elsewhere [17].

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