Selective Photon-Stimulated Desorption of Hydrogen from GaAs Surfaces

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(Received 11 August 1999)

Photon-stimulated desorption of H^+ from hydrogenated GaAs (110) and (100) surfaces was studied as a function of photon energy. Distinct peaks, observed around As $3d$ core-level binding energy for desorption from the GaAs (100) surface and in the As $3d$ and Ga $3p$ region for desorption from the GaAs (110) surface, show a striking similarity with the fine structure (spin-orbit splitting) measured in the photoemission from As $3d$ and Ga $3p$ levels. These results provide clear evidence for direct desorption processes and represent a basis for selective modification of hydrogenated GaAs surfaces.

Desorption of ions from surfaces under photon and electron irradiation, known as photon-stimulated desorption (PSD) and electron-stimulated desorption (ESD), respectively, has been recognized as a powerful technique for the investigation of the local electronic structure and bonding of adsorbed species [1]. In both PSD and ESD, the escape probability of ions created below the surface is very small, due to the efficiency of the neutralization process, and only ions formed in the surface region are detected. Indeed, we have demonstrated recently by PSD of hydrogen ions from hydrogenated diamond films that ion desorption can be more surface sensitive than electron emission [2].

The hydrogenated GaAs surface is an ideal system for studying chemisorption processes and rearrangements of surface atoms [3,4]. Many surface sensitive techniques, ranging from high-resolution electron-energy-loss spectroscopy [3] to scanning tunneling microscopy [4], have been employed to study the interaction of atomic hydrogen with GaAs surfaces. While there are several reports on ESD from GaAs surfaces in the literature [1,5,6], few reports on PSD from GaAs have been published to date [1]. To the best of our knowledge, there is only one report of PSD of H^+ from GaAs [7], dealing with the H^+ desorption from GaAs:H_2O in the valence-band excitation region. In the present Letter we report, for the first time, on PSD of H^+ from GaAs around core-level energies of Ga and As atoms.

Desorption induced by core-level excitations may involve direct and indirect processes. A direct process is initiated by the Auger decay of a core hole, created by photon bombardment, which may lead to localized repulsive states in the bonding orbitals [1,8,9]. On the other hand, an indirect desorption process is initiated by the secondary electrons (released during an Auger process) that induce the valence-band excitations followed by the desorption of positive ions [1].

The mechanism of stimulated desorption and the contribution of direct and indirect processes may be studied in some detail by comparing the positive ion yield, as the function of photon energy, and the photoabsorption recorded by measuring the partial electron yield for selected electron kinetic energies [10]. In addition, the chemical shifts in photoemission spectra may provide the evidence for the bonding site of desorbed ions [11]. Unfortunately, neither of these methods works on hydrogenated GaAs surfaces around the As $3d$ edge. The photoabsorption measurements are hindered around As $3d$ edge by overlapping with the valence-band photoemission. On the other hand, there is very little change in As core-level binding energies due to the hydrogen bonding [12,13]. In this Letter we show, for the first time, that the direct desorption mechanism in such cases can be identified by comparing the PSD data from differently terminated surfaces. Further, we compare the PSD yield of H^+ with the core-level photoelectron spectra of Ga and As. This comparison shows for the first time for a covalent system a close similarity between the PSD yield of positive ions and the photoelectron spectra around core levels. This provides direct evidence for a desorption process induced by ionization of core levels of bonding surface atoms. However, in a covalent system, such as GaAs:H, the two holes created by the Auger process must remain localized in the bonding orbital for a sufficiently long time to provide desorption of positive ions [9]. Finally, the results presented in this Letter suggest

the possible use of synchrotron radiation for bond-selective chemistry and modification of hydrogenated surfaces.

The GaAs samples were grown by molecular beam epitaxy (MBE) using semi-insulating GaAs (110) and (100) substrates. An undoped GaAs buffer layer approximately 0.25 μm thick was grown on each substrate, having either the nonpolar (110) surface with equal number of Ga and As atoms or the polar (100) surface terminated with As. The samples were capped with an amorphous As layer and transported under an Ar atmosphere to the synchrotron radiation facility at LURE. All measurements were performed in an ultrahigh vacuum (UHV) chamber connected to the beam line SA23 of Super-Aco at LURE, which delivers photons in the 35–125 eV range. The UHV chamber was equipped with a hemispherical electron analyzer (CLAM) for photoemission studies and a high sensitivity quadrupole mass analyzer (Riber MIQ 156) for ion detection. The arsenic cap was removed in the UHV chamber by heating each sample to ~400 °C. This procedure is known to produce a surface of quality similar to an as-grown MBE surface, with possibly a small amount of As from the cap remaining on the surface [14]. The clean surfaces were exposed to 3×10^4 L (langmuirs) of molecular hydrogen. As H_2 does not adsorb on the surface, atomic hydrogen was produced by dissociation of H_2 at a hot filament placed ~5 cm away from the sample surface. The hydrogen exposure used in this study was below the level causing a highly disordered surface [4] and the saturation coverage of polar surfaces [12].

Figure 1 illustrates the effect of hydrogen adsorption on the GaAs surface. The mass spectrum of Fig. 1 was obtained from the hydrogenated GaAs (110) surface by collecting positive ions during irradiation with 115.7 eV photons. The peaks at 1 and 19 amu represent hydrogen and fluorine, respectively. The hydrogen peak intensity after hydrogenation is about 300 times higher than from the clean surface. The ever present F^+ peak is due to the extremely high ionization probability of fluorine which makes the F^+ peak observable even from surfaces which show no detectable F by other surface sensitive techniques [1]. The samples were also characterized before and after hydrogenation by the UV photoemission spectroscopy
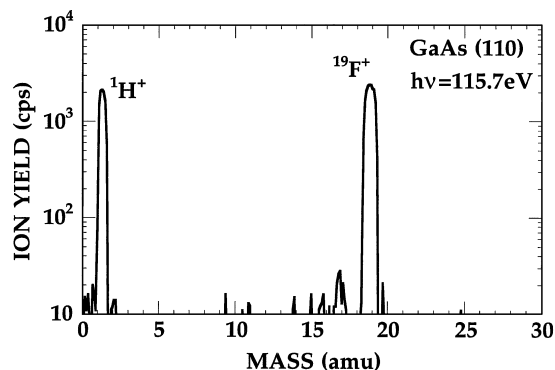
(UPS) taken by synchrotron radiation. The UPS spectra (not shown) are very similar to the spectra from clean and hydrogenated GaAs surfaces to be found in the literature [12,15]. The difference between the UPS spectra before and after hydrogenation shows two distinct peaks indicating removal of the surface states, which existed on the clean GaAs surfaces, by hydrogen bonding.

The PSD measurements were performed in the 35–120 eV range, which covers As $3d$ and Ga $3p$ core-level binding energies. The PSD spectrum of H^+ from hydrogenated GaAs (100) surface is shown in Fig. 2(a) as a function of photon-beam energy. For these low energy measurements, the photon beam was filtered by an Al filter to remove the contributions of higher-order radiation to the spectrum. From this polar (As-terminated) surface
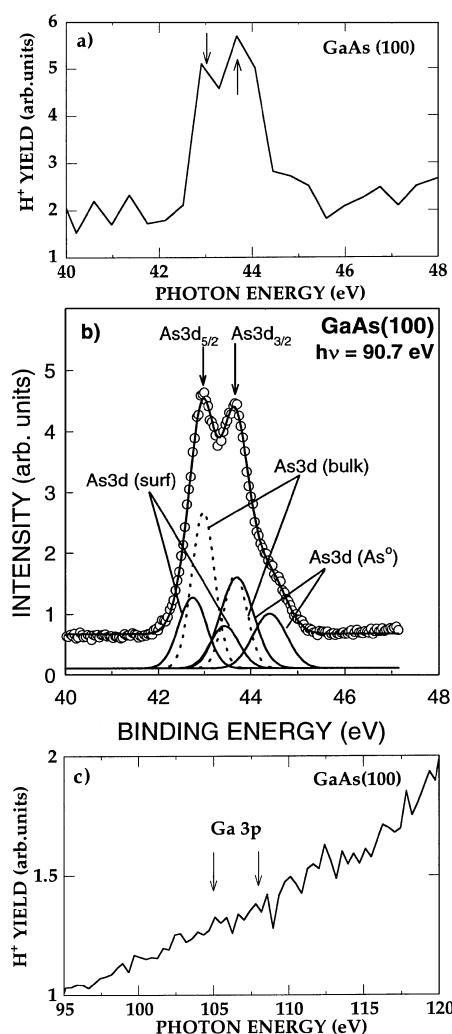

FIG. 2. (a) Normalized PSD yield of H^+ from a hydrogenated GaAs (100) surface as a function of photon energy around As $3d$ core-level binding energy. (b) As $3d$ photoemission spectrum from the same surface together with the SO deconvolution. Spin-orbit splitting of the $3d$ level is indicated by arrows, and the three pairs of SO doublets originate from the surface, bulk, and residual (As°) emission. (c) Desorption yield of H^+ around Ga $3p$ core-level binding energy.

FIG 1. PSD positive-ion mass spectrum from a hydrogenated GaAs (110) surface.

we detected two resonantlike peaks at 43 and 43.7 eV, corresponding to the As $3d$ core-level binding energies [indicated by arrows in Fig. 2(a)] [16]. No thresholds or peaks were observed from this surface at higher energies around the binding energy of the Ga $3p$ level as shown in Fig. 2(c). In Fig. 2(b) we show the photoelectron spectrum (open circles) around the As $3d$ level, obtained by synchrotron radiation spectroscopy. This spectrum is shown with reference to the conduction-band minimum (CBM) to be directly compared to the PSD of H^+ (the peaks in these curves correspond to the $3d \rightarrow$ CBM transitions). The photoemission spectrum in Fig. 2(b) clearly shows the fine structure caused by the spin-orbit (SO) splitting of corresponding core levels indicated by arrows. There is a striking similarity between the shape and width of H^+ PSD curve and corresponding photoelectron spectrum. Even the fine details in the photoelectron spectra (i.e., the SO splitting of corresponding core levels and a kink at 44.5 eV) are reflected in the PSD of H^+. To the best of our knowledge, the close similarity between the PSD yield of ions and the photoelectron spectra around core levels has never been reported previously for covalent systems such as GaAs:H. The close correspondence in shape and energy position between the H^+ yield and the photoelectron emission strongly suggests that the excitation of core electrons on bonding As atoms plays a dominant role in desorption of H^+. There are two possible mechanisms which can account for the photodesorption of positive ions closely following the ionization of core levels. The first is an indirect desorption mechanism that involves the bulk excitations. The second mechanism is a direct process involving the surface excitations.

The contribution of indirect processes (i.e., the photon-induced ESD) is believed to be small, but may dominate the total yield in those cases when the other desorption mechanisms are suppressed [10]. The minimum energy required to desorb H^+ from GaAs is 16–19 eV [7]. As the secondary electrons with such high kinetic energies do exist in secondary electron spectra from GaAs, an indirect process is a viable option. In general, an indirect mechanism can be identified by comparing the PSD yield with the total absorption coefficient and measuring the shift of PSD threshold caused by the chemical shift of core levels due to the surface bonding [10,11]. Neither of these methods works on hydrogenated GaAs surfaces around the As $3d$ edge: the photoabsorption measurements overlap with the UPS spectra and the As core-level binding energy exhibits no or very little shift due to the hydrogen bonding. For example, no chemical shifts were observed for As $3d$ and Ga $3d$ core-level binding energies upon hydrogenation [13] or shifts of only 0.12 and 0.03 eV were observed for As and Ga levels, respectively [9]. Our measurements, estimated to be accurate to within 0.2 eV around the As $3d$ level, reveal no change in binding energy after hydrogenation.

In the case of GaAs, the comparison of desorption yields from differently terminated surfaces may help to identify the desorption mechanism. For the first time, we carried out the PSD measurements of H^+ on both a polar, As-terminated surface (shown in Fig. 2) and a nonpolar surface with equal number of Ga and As atoms (see Fig. 3). As shown in Fig. 3(a), the resonantlike desorption of H^+ from the nonpolar surface occurs at both the Ga $3p$ edge (at 105 and 108 eV) and As $3d$ edge. In Fig. 3(b) we show the photoemission spectrum from the GaAs (110) surface around the Ga $3p$ edge which exhibits the characteristic SO splitting [16]. Once again, the structure in the H^+ yield, this time at the Ga $3p$ edge [Fig 3(a)], is closely related to the SO splitting of that level. We point out here that the photoemission measurements around the Ga $3p$ level are just at the edge of the energy range of Super-Aco beam line SA23; thus the photoemission spectrum was taken by using 250 eV photons from another beam line.

The results shown in Figs. 2 and 3 provide clear evidence for a direct process in desorption of H^+. Namely, the photons of 40–120 eV can ionize both As and Ga core levels, thus producing secondary electrons of sufficient energy to induce an ESD process. Therefore, if an indirect process accounts for the desorption of H^+, the PSD yield from both surfaces should exhibit a change at both As and Ga edges. Our experiments reveal that H^+ desorbs from only As atoms on a polar, As-terminated surface. The absence of the Ga edge in this case clearly indicates that the
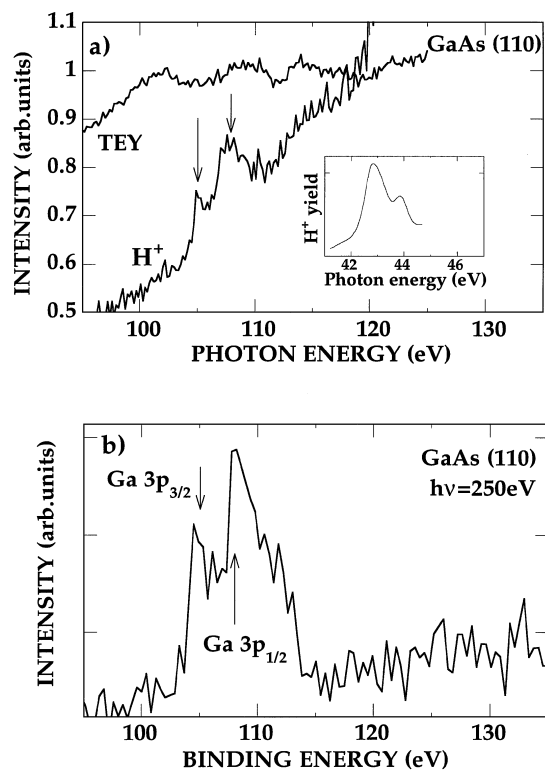

FIG. 3. (a) Normalized PSD yield of H^+ from a hydrogenated GaAs (110) surface as a function of photon energy around Ga $3p$ edge. TEY curve for 40 eV photoelectrons is also shown for the same energy range. Inset shows the H^+ yield (smoothed) around As $3d$ edge. (b) Ga $3p$ photoelectron spectrum showing the spin-orbit splitting.

photoelectrons formed on Ga sites below the As dimers are not effective in H^+ desorption. Further, the photoabsorption measurements around the Ga $3p$ edge [represented by the total electron yield (TEY) curve in Fig. 3(a)] do not exhibit the fine structure observed in PSD of H^+. Thus, it is reasonable to conclude that the indirect mechanism does not play a significant role in the resonantlike desorption of H^+. The main contribution comes from a direct desorption process initiated by ionization of As-H and Ga-H surface complexes.

Turning now to the direct mechanism in photodesorption we note that, in a highly ionic system, core-level ionization of a cation and subsequent interatomic Auger relaxation of the core hole leaves, in general, two or three holes in the bonding orbital. The bond breaking and desorption of positive ions results from the reversal of the Madelung potential [Knotek-Feibelman (KF) mechanism] [8]. In this case, a sharp onset in positive ion yield should correlate with the excitation energy of the core level. On the other hand, Auger decay of a core hole in a covalent bond may lead to a localized two-hole ($2h$) final state in the bonding orbital [9]. If the lifetime of this state is sufficiently long, desorption of positive ion may occur via unscreened hole-hole repulsion. Localization of the valence holes results only if the hole-hole repulsion energy U is greater than some appropriate covalent interaction or bandwidth Γ [9].

The bonding of H to Ga and As atoms is predominantly covalent and the KF condition for maximal valency is not present for hydrogenated GaAs surfaces. The $2h$-localization model is apparently favored. The bandwidth Γ in GaAs is around 7 eV [17] and if we assume an effective hole-hole repulsion of $8-10$ eV [9], the condition $U > \Gamma$ is satisfied and the two valence holes remain localized in bonding orbitals long enough for desorption to occur. However, the broad bandwidth in GaAs (reflecting a large overlap of wave functions of the atoms in the solid) increases the possibility of charge transfer between atoms, i.e., the hole hopping decay rate which prevents the high yield in ion desorption. Therefore, we suggest the following explanation for photodesorption of H^+ from GaAs in the energy range studied in this work. Core-hole formation in M shells of As ($3d$ level) and/or Ga ($3p$ level) initiates an interatomic Auger decay process involving covalent As-H and Ga-H bonds. This process may lead to a localized $2h$ final state in the bonding orbital. The lifetime of this state is sufficiently long (of the order of 10^{-13} s [1]) that desorption of H^+ may occur via unscreened hole-hole (Coulombic) repulsion.

The desorption measurements of H^+ also reveal the bonding sites of hydrogen atoms at the outermost GaAs surface. This provides a basis for chemically selective modification of surfaces. By tuning the excitation energy to the core-level binding energy of As or Ga, hydrogen can be selectively removed from the surface. Even desorption from the same types of atomic sites can be selective. In Fig. 2(b) we further explore this point. Here, we decon-

volute the As $3d$ photoemission peak into three components originated either from the surface and bulk emission or from the emission from residual As. Each component exhibits characteristic $3d_{5/2}$-$3d_{3/2}$ SO splitting of 0.7 eV and a branch ratio of 0.6 [14]. Comparison of Figs. 2(a) and 2(b) makes it clear that the H^+ desorption from the As terminated GaAs surface originates not only from the H bonded to As from GaAs, but from the remaining As from the cap as well. The selective removal of hydrogen (from GaAs or residual As) may be obtained by tuning the synchrotron radiation to the energy corresponding to different peaks in Fig. 2(a).

In conclusion, the difference in the yield of H^+, photodesorbed from hydrogenated GaAs (100) and (110) surfaces of different termination, provides evidence for a direct desorption process. Further, the comparison between the PSD and the photoemission spectra shows that the PSD of H^+ is initiated by ionization of core levels of bonding atoms. The site specific desorption and fine structure of the PSD signal represents a basis for selective modification of hydrogenated surfaces. By tuning synchrotron radiation to particular energy, hydrogen atoms bonded to a specific site may be selectively removed from the surface.

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