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PHOTON-STIMULATED DESORPTION OF HYDROGEN IONS FROM SEMICONDUCTOR SURFACES: EVIDENCE FOR DIRECT AND INDIRECT PROCESSES

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Dedicated to Professor Boran Leontić on the occasion of his 70th birthday

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Photon-stimulated desorption of positive hydrogen ions from hydrogenated diamond and GaAs surfaces have been studied for incident photon energies around core-level binding energies of substrate atoms. In the case of diamond surfaces, the comparison between the H^+ yield and the near edge X-ray absorption fine structure (NEXAFS) for electrons of selected kinetic energies reveals two different processes leading to photodesorption: an indirect process involving secondary electrons from the bulk and a direct process involving core-level excitations of surface carbon atoms bonded to hydrogen. The comparison of H^+ photodesorption and electron photoemission as the function of photon energy from polar and non-polar GaAs surfaces provides clear evidence for direct desorption processes initiated by ionisation of corresponding core levels of bonding atoms.

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1. *Introduction*

The bombardment of a sample surface by low-energy photons can induce desorption of neutral and ionic species from the surface, particularly if the surface contains an adsorbed layer [1]. This effect, known as photon-stimulated desorption (PSD), is a consequence of primary electronic excitations whose relaxation causes bond breaking and desorption. Several different models have been proposed for explanation of desorption from ionic and covalent surfaces. Although these differ in details, all models consider valence or core electronic excitations, followed by rapid electronic rearrangement to repulsive states, as the driving force for desorption [1]. It now appears that, in many cases, the valence mechanism plays only a minor role in positive-ion desorption, as a growing number of experiments show dominant onsets in desorption yield of positive ions at energies related to the excitation of core levels [2,3].

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 localised repulsive states in the bonding orbitals [4]. 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 [5]. The contribution of indirect processes is believed to be small, but may dominate the total yield in those cases when the other desorption mechanisms are suppressed [6].

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 near edge X-ray adsorption fine structure (NEXAFS) recorded by measuring the partial electron yield (PEY) for selected electron-kinetic energies. We employed this method to study desorption of positive hydrogen ions from different hydrogenated semiconductor surfaces. For some of them, however, the NEXAFS measurements may be hindered around a particular core-level by overlapping with the valence band photoemission. In order to overcome this problem in the case of GaAs, we have carried out the PSD measurements on differently terminated GaAs surfaces.

This research has also been driven by the great technological importance of hydrogenated semiconductor surfaces: understanding the chemistry and bonding of hydrogen on semiconductor surfaces is crucial for both wafer cleaning and polishing and for epitaxial growth where hydrogen is thought to inhibit epitaxy [7]. We also point out here that the characterisation of hydrogen on semiconductor surfaces represents a very difficult experimental problem. Commonly used surface sensitive techniques, such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), are not sensitive to hydrogen. Some other techniques, such as infrared spectroscopy, that are sensitive to hydrogen bonding, lack surface sensitivity. On the other hand, it is well known that the ion photodesorption represents a very sensitive surface probe for the investigation of the local electron structure and bonding of adsorbed species [1]. From the analytical point of view, it is important to explore the desorption mechanism of positive ions under photon bombardment and the sensitivity of PSD for hydrogen adsorbed on semiconductor surfaces.

2. *Experimental*

Polycrystalline 10 μm thick diamond films were deposited on silicon substrates by the hot filament chemical vapour deposition (CVD) method, using a system described previously [8]. The Raman spectrum measured for these films shows only the characteristic diamond line at 1333 cm^{-1}. No additional lines associated with amorphous carbon or graphite were measured in the Raman spectrum. Scanning-electron-microscopy (SEM) examination of the films indicated that they were continuos and composed of crystallites of 2 –3 μm in size. Auger analysis of the films shows that their surface was free of oxygen and other impurities ($<$ 0.05 at.%). The surface of the as deposited films was terminated by atomic hydrogen. This was determined ex-situ by temperature programmed desorption (TPD) measurements of the as deposited films.

The GaAs samples were grown by molecular beam epitaxy (MBE) using semi-insulating GaAs (110) and (100) substrates. Following thermal oxide removal, an undoped GaAs buffer layer approximately 0.25 μm thick was grown on each substrate, having either the non-polar (110) surface with equal number of Ga and As atoms or the polar, As terminated (100) surface. The samples were then allowed to cool under an As_2 flux while a liquid nitrogen cooled finger contacted the substrate mounting block. Over a period of some hours, an amorphous arsenic layer capped the surface, thus protecting it against degradation.

All measurements were performed in an ultra high vacuum (UHV) chamber connected to either the synchrotron beam-line SA72 or SA23 of Super-Aco at LURE, which delivers photons in the 150 – 600 eV or 35 – 125 eV range, respectively. The UHV chamber is equipped with a hemispherical electron analyser (CLAM) for photoemission studies and a high-sensitivity quadrupole mass analyser (Riber MIQ 156) for ion detection. A gas manifold and an activation set-up was added for adsorption measurements.

The arsenic cap on GaAs samples was removed in the UHV chamber by heating each sample to about 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 [9]. The clean surfaces were exposed to 3×10^4 L (langmuir) of molecular hydrogen ($1\,\mathrm{L} = 10^{-6}$ torr of $H_2 \times 1$ s, 1 torr = 133 Pa). As H_2 does not adsorb on the surface, atomic hydrogen was produced by dissociation of H_2 at a hot filament placed about 5 cm away from the sample surface. The hydrogen exposure used in this study was below the level causing a highly disordered surface [10].

3. *Results and discussion*

3.1. *Photodesorption from diamond films*

We start with the photodesorption from diamond surfaces, taken from Ref. [16], to illustrate the standard procedure in the determination of desorption channels. PSD of positive hydrogen ions and the NEXAFS spectrum from the hydrogenated diamond surface, measured by photons in the 280 – 340 eV energy range, are shown in Fig. 1. The NEXAFS spectrum was taken for secondary electrons of kinetic energy of 8 eV, that are more bulk sensitive [12], and it basically represents the total electron yield (TEY).

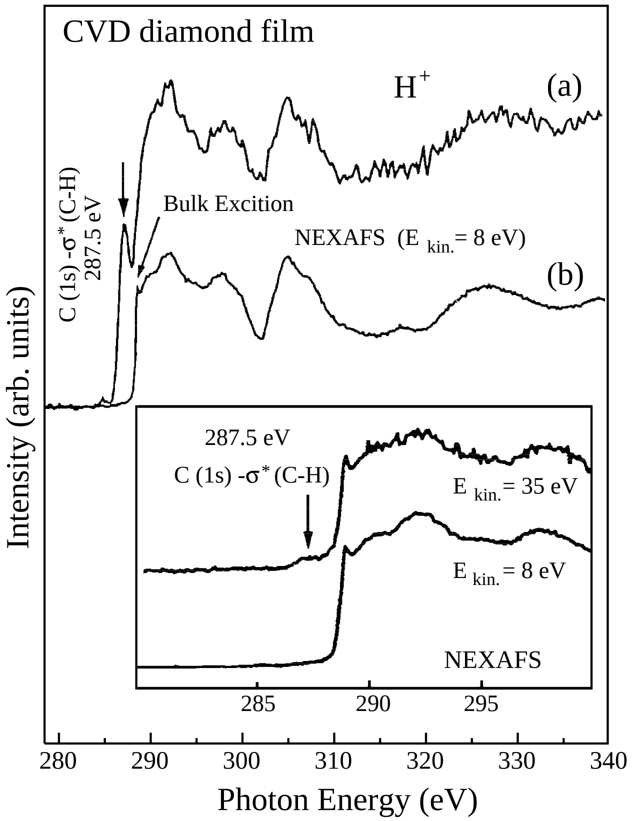

Fig. 1. a) Desorption yield of H^+ *from the diamond film as a function of incident photon energy and b) the NEXAFS spectrum taken for 8* eV *secondary electrons from the same surface. The inset shows the NEXAFS spectra of 8* eV *and 35* eV *electrons.*

The NEXAFS spectrum in Fig. 1 displays a threshold at 289 eV followed by a very sharp peak at 289.2 eV and broader peaks at higher photon energies. The dip at 302.4 eV is associated with the absolute second band gap of diamond and the sharp peak at 289.2 eV with a core exciton [13].

The H^+ desorption yield displays features similar to those of the NEXAFS with an additional sharp structure at 287.5 eV, 2 eV below the threshold of the NEXAFS spectrum (see Fig. 1a). The comparison between the PSD and NEXAFS data indicates that the H^+ yield consists of a signal proportional to the TEY, with a threshold at about 289 eV, superimposed on a resonance at 287.5 eV.

3.2. Photodesorption from GaAs *surfaces*

The PSD of H^+ from GaAs surfaces was measured using photons in the 35 – 120 eV energy 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. 2a as a function of the photon-beam energy. From this polar (As-terminated) surface, we detected two well resolved resonant-like peaks in PSD of H^+ at 43 eV and 43.7

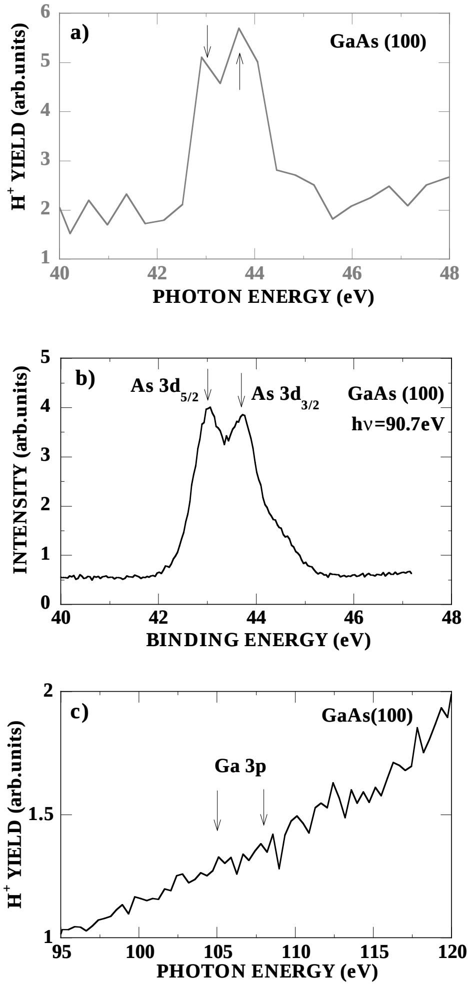

Fig. 2. a) Normalised desorption yield of H^+ *from a hydrogenated* GaAs *(100) surface as a function of photon energy around* As 3d *core-level binding energy. b)* As 3d *photoemission spectrum from the same surface. Spin-orbit splitting of the* 3d *level is indicated by arrows. c) Desorption yield of* H^+ *from the same surface around* Ga 3p *core-level binding energy.*

eV, corresponding to the As 3d core-level binding energies (indicated by arrows in Fig. 2a) [11]. 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. 2c. In Fig. 2b, we show the photoelectron spectrum 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. 2b 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 of the 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^+.

3.3. Direct and indirect processes in PSD of H^+

The results shown in Figs. 1 and 2 reveal two distinct processes in PSD of H^+ which can account for the photodesorption of positive ions closely following the ionisation of core levels. The first is an indirect desorption process that involves valence excitations at the surface induced by secondary photoelectrons. The second mechanism is a direct process, in which a core-hole formation initiates an Auger decay followed by desorption of positive ions.

The desorption of H^+ from diamond surfaces (Fig. 1), taken from Ref. [16], represents a case showing both direct and indirect desorption channels. The direct process is characterised by the resonance at 287.5 eV and does not show the features of the TEY (see Fig. 1). The weak structure at 287.5 eV has been also observed in NEXAFS taken for 35 eV electrons (see inset to Fig. 1), which are more surface sensitive [12], and it has been previously assigned to a C(1s) $\rightarrow \sigma^*$ (C-H) resonance [14]. The appearance of the 287.5 eV peak in the surface sensitive NEXAFS mode is, therefore, most probably associated with the presence of C-H species on the diamond surface. Consequently, the resonance at 287.5 eV in the PSD of H^+ may be also associated to the core-level excitations of surface carbon atoms bonded to hydrogen atoms. In Ref. 16, we suggested the following mechanism for this process. The ionisation of the 1s core-level of carbon atom bonded to hydrogen initiates an Auger transition leading to the emission of a C(KLL) Auger electron with the kinetic energy of about 270 keV and formation of two localised valence-band holes [4]. These localised two-hole states may cause the bond breaking and the emission of H^+ through the charge separation as the most likely way to relax the large hole-hole repulsive interaction.

On the other hand, the indirect process in desorption of H^+ from diamond surfaces is generated by the bulk excitations, i.e. by the large flow of secondary electrons which are released in the decay process of C(1s) core holes created by photon bombardment. The minimum energy required to desorb H^+ from the diamond surface (consisting of the sum of the C-H bond energy and the ionisation energy of H, reduced by the electron affinity of the hydrogenated surface) is at least

18 eV and some multielectron valence excitations may account for desorption of H^+ [15,16].

Turning now to the desorption of H^+ from GaAs surfaces (Fig. 2), we note once again that, in general, an indirect mechanism can be identified by measuring the energy dependence of the total absorption coefficient, represented by the TEY (as shown in Fig. 1 for the desorption from hydrogenated diamond films), while the further information can be obtained from the shift of PSD threshold caused by the chemical shift of core levels due to the surface bonding [17]. Neither of these methods works on hydrogenated GaAs (100) surface around the As 3d edge. The TEY measurements are hindered around the As 3d edge by overlapping with the valence band photoemission. On the other hand, there is no (or very little) change in As core-level binding energies due to the hydrogen chemisorption on the surface [18]. In order to identify the desorption mechanism of H^+ from GaAs surfaces, we applied a new approach based on comparison of desorption yield from differently terminated surfaces.

A compound matrix, such as GaAs, exhibits different surface termination for different crystal orientation, and the PSD from different surfaces may provide the clue for the desorption mechanism. Therefore, we carried out the PSD measurements on both the polar (As terminated) GaAs (100) surface (Fig. 2) and the non-polar GaAs (110) surface with equal number of Ga and As atoms (Fig. 3). In contrast to the GaAs (100) surface, the resonant-like desorption of H^+ from the GaAs (110) surface was detected at both the Ga 3p edge (at 105 eV and 108 eV, see Fig. 3a) and the As 3d edge. In Fig. 3b, we show the photoemission spectrum from the GaAs (110) surface around the Ga 3p edge which exhibits the characteristic SO splitting [11]. Comparison of the PSD yield of H^+ with the photoemission spectrum confirms, once again, that the structure in the H^+ yield at the Ga 3p edge is related to the SO-splitting of that level.

The results shown in Figs. 2 and 3 provide a clear evidence for a direct process in desorption of H^+ from GaAs surfaces. Namely, if an indirect process accounts for the desorption of hydrogen, the PSD yield should exhibit a change at both As and Ga edges on both surfaces, as photons of 40 – 120 eV ionise both As and Ga core levels, thus producing secondary electrons of sufficient energy to induce an electron-stimulated desorption process. For the low hydrogen coverage, however, hydrogen desorbs only from As atoms on a polar, As-terminated GaAs surface, but from both Ga and As atoms on a non-polar GaAs surface with equal numbers of Ga and As atoms. The absence of the Ga edge in the H^+ yield in Fig. 2c clearly indicates that the photoelectrons formed on Ga sites are not effective in H^+ desorption. Further, the fine structure in PSD of H^+ has not been found in our photoabsorption measurements around the Ga 3p edge (represented by the TEY curve in Fig. 3a). Thus, it is reasonable to conclude that the indirect mechanism does not play a significant role in the resonant-like desorption of H^+ from hydrogenated GaAs surfaces. The main contribution comes from a direct desorption process initiated by ionisation of As-H and/or Ga-H surface complexes. The core-hole formation in the M-shell of As (3d level) and/or Ga (3p level) initiates an interatomic Auger decay process which may produce a localised two-hole final state in the bonding orbital. The lifetime of that state is sufficiently long (about 10^{-13} s [5]) and desorption of H^+ may occur via unscreened hole-hole (Coulombic) repulsion.

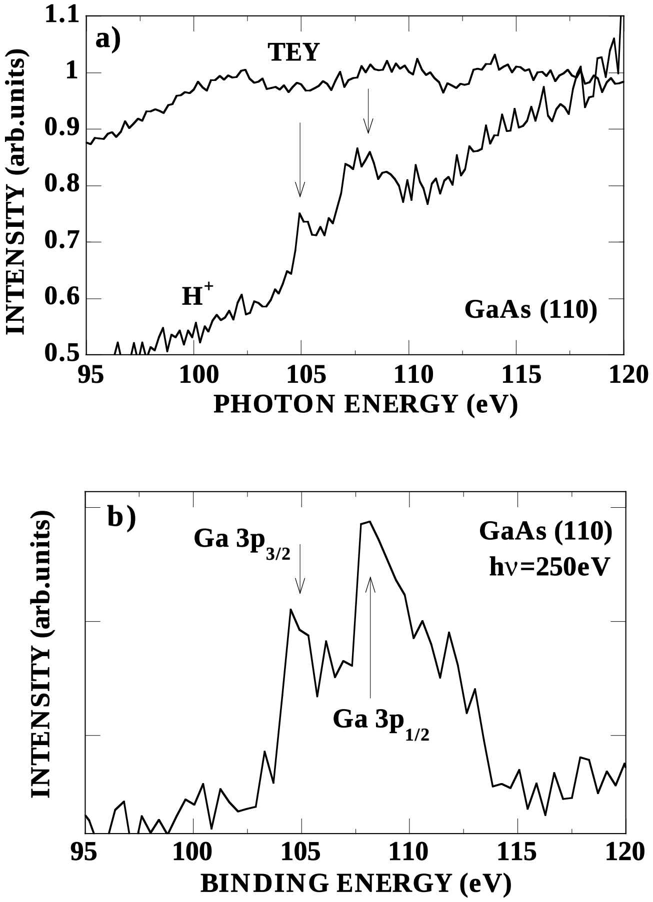

Fig. 3. a) Normalised desorption yield of H^+ *from a hydrogenated* GaAs *(110) surface as a function of photon energy around the* Ga 3p *core-level binding energy. Total electron yield (TEY) curve for 40* eV *photoelectrons is also shown for the same energy range. b)* Ga 3p *photoelectron spectrum showing the spin-orbit splitting.*

4. Conclusion

We have shown that the PSD of positive hydrogen ions from hydrogenated semiconductor surfaces may proceed via two distinctive processes: the first one results from bulk excitations and involves the secondary electrons, while the second one results from surface excitations and involves the Auger decay of core holes. Our results demonstrate that the mechanism of the desorption process can be revealed by the comparison of the PSD-threshold measurements with the photoemission and NEXAFS measurements around the core-level binding energies or by the comparison of photodesorption from differently terminated surfaces.

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FOTONIMA STIMULIRANA DESORPCIJA VODIKOVIH IONA IZ POLUVODIČKIH POVRŠINA: DOKAZI IZRAVNIH I POSREDNIH PROCESA

Proučavali smo fotonima stimuliranu desorpciju pozitivnih iona vodika iz hidrogeniziranih površina dijamanta i GaAs, za fotone energije oko energija vezanja unutarnjih elektrona atoma podloge. U slučaju površine dijamanta, usporedba prinosa H^+ i fine strukture blizu-rubne apsorpcije X-zračenja (NEXAFS) za elektrone odabranih kinetičkih energija otkriva dva različita procesa koji uzrokuju fotodesorpciju: posredan proces uz sudjelovanje sekundarnih elektrona iz osnovnog materijala, i izravan proces uzrokovan uzbudom unutarnjih elektrona površinskih atoma ugljika vezanih na vodik. Usporedba fotodesorpcije H^+ i emisije elektrona u ovisnosti o energiji fotona iz polarnih i nepolarnih površina GaAs daje jasne dokaze za izravne procese desorpcije uzrokovane ionizacijom odgovarajućih unutarnjih stanja veznih atoma.