

Electronic structure of H/Ge(111)1×1 studied by angle-resolved photoelectron spectroscopy

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The electronic structure of H/Ge(111)1×1 was investigated using angle-resolved photoelectron spectroscopy. Spectra were measured along the high-symmetry lines of the 1×1 surface Brillouin zone. In the $\bar{\Gamma}-\bar{K}-\bar{M}$ direction, two surface states, labeled a and a' , were found in the lower and upper band-gap pockets. The a and a' surface states are associated with the Ge-H bonds and the Ge-Ge backbonds, respectively. In the $\bar{\Gamma}-\bar{M}$ direction, only the Ge-H surface state, a , can be identified. It is found in the band-gap pocket around the \bar{M} point. The two hydrogen-induced surface states on H/Ge(111)1×1 show strong similarities with the corresponding surface states on H/Si(111)1×1. Results from H/Ge(111)1×1 and H/Si(111)1×1 are compared in this Brief Report.

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Hydrogen adsorption on semiconductor surfaces such as Si and Ge has been of great interest in surface science. It results in an opportunity to study the unreconstructed surface and to determine the effects of reconstruction on the properties of the surface. Hydrogen changes the structural and electronic properties of the surfaces on which it is adsorbed. For instance, the surfaces become passivated which means that they are less reactive than the clean surfaces due to capping of the dangling bonds by the hydrogen atoms.

The unreconstructed (111)1×1 surfaces of Si and Ge have similar bond configurations which allows for a direct comparison of the electronic structure of these two surfaces. The electronic properties of the H/Ge(111)1×1 surface have not been explored to the same extent as those of the H/Si(111)1×1 surface. A significant number of studies involving hydrogen adsorption on Si(111) has been performed by several research groups.¹⁻⁷ As a result of these investigations, the electronic structure of the H/Si(111)1×1 is already well established. Two surface states due to Si-Si backbonds and Si-H bonds have been identified. Pandey¹ performed a realistic tight-binding calculation for the chemisorption of hydrogen on Si(111) and Ge(111) resulting in surface energy bands and local density of states. The presence of a surface-state band that corresponds to the Si-H (Ge-H) bond is the most obvious feature in the electronic structure. Landmark *et al.*² studied the electronic structure of the 1×1 monohydride surface in detail using angle-resolved photoelectron spectroscopy (ARPES). Two surface-state bands were identified that showed very good agreement with the Si-H and Si-Si backbond states obtained in the surface band-structure calculation.¹ Similar ARPES spectra have also been published by Hricovini *et al.*⁷ and Karlsson *et al.*⁴ Also Gallego *et al.*³ studied the valence-band structure of the H/Si(111)1×1 surface and they confirmed the presence of the two surface states in agreement with previous experimental^{2,4,7} and theoretical studies.^{1,5,6} A sharp feature, labeled b , located at 4.3 eV below the valence-band maximum (VBM) at the \bar{K} point, i.e., between the a and a' peaks, was reported in Ref. 3. The energy position and dispersion of this structure closely resemble what have earlier been reported for a direct-transition structure.^{9,10} However, based on the small dispersion, <0.25 eV, in the k_{\perp} direction (in the

energy range of 22–36 eV) and on the results of a tight-binding calculation they identified the structure as due to a surface resonance (SR) state.

Only a few photoemission studies have been performed on the H/Ge(111)1×1 surface. Angle-resolved measurements were done by Bringans and Höchst⁸ on the hydrogen-covered Ge(111) surface and they observed a strong hydrogen-induced peak at –5 eV relative to the VBM. Wachs *et al.*¹¹ performed a normal-emission study recording spectra for H/Ge(111)1×1 at different photon energies in order to study the effect on the surface states of the Ge(111)c(2×8) surface upon hydrogen adsorption.

A detailed study of the electronic structure of the H/Ge(111)1×1 surface has not been done before. In this Brief Report, we present ARPES data in order to establish the surface band structure of H/Ge(111)1×1. When relevant, comparisons are made with the electronic structure of H/Si(111)1×1.

The experiments were performed at beam line 33 at the MAX-lab synchrotron radiation facility in Lund, Sweden. Angle-resolved valence-band spectra were obtained with a total-energy resolution of ~70 meV and an angular resolution of $\pm 2^{\circ}$. An Sb-doped ($\rho=3 \Omega \text{ cm}$) Ge(111) sample was cleaned by ion sputtering (Ar⁺, 0.5 kV). Thermal annealing for several minutes at ~600 °C was done in order to recover the crystalline structure. This procedure resulted in a well-ordered surface as evidenced by sharp c(2×8) low-energy electron-diffraction (LEED) spots. Hydrogen exposure was done in a preparation chamber that had a base pressure of $<1 \times 10^{-10}$ Torr. To verify the quality of the hydrogen gas it was checked by a mass spectrometer. The molecular hydrogen was dissociated into atomic hydrogen by a tungsten filament that was heated to ~1800 °C. While keeping the sample at ~250 °C it was exposed to 5000 L of H₂ facing the hot filament. This resulted in an unreconstructed surface as evidenced by sharp 1×1 diffraction spots. The sample was then immediately transferred to the analysis chamber in order to collect photoemission data at a sample temperature of 100 K in this case. For comparison, we have included a spectrum of a H/Si(111)1×1 surface prepared by a 15 000L H₂ exposure in front of the heated filament, while keeping the sample at ~400 °C.

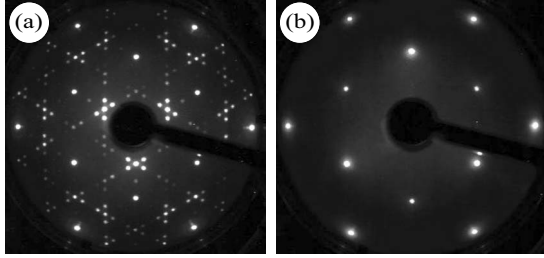


FIG. 1. LEED pattern of (a) the clean surface showing sharp $c(2 \times 8)$ diffraction spots recorded at room temperature and (b) the H-exposed surface showing 1×1 diffraction spots obtained at 100 K. Both LEED patterns were recorded with an electron energy of 98 eV.

Figure 1(a) shows the LEED pattern of the clean surface obtained with an electron energy of 98 eV at room temperature. The sharp $c(2 \times 8)$ diffraction spots confirm that the surface has a well-ordered periodicity. The 1/2- and 1/8-order spots can be observed in the LEED pattern. It also shows weak 1/4-order spots. Figure 1(b) is the LEED pattern obtained after the hydrogen exposure recorded with an electron energy of 98 eV at 100 K. The diffraction pattern exhibits sharp 1×1 spots.

Since Si(111) and Ge(111) surfaces are very similar in terms of the bond configurations, a comparison of the electronic structures of the less studied H/Ge(111) 1×1 surface and the well established H/Si(111) 1×1 is therefore possible. Figure 2(a) shows a valence-band spectrum of the H/Si(111) 1×1 surface obtained along the $\bar{\Gamma}-\bar{K}-\bar{M}$ azimuth at an emission angle of 38° , which corresponds to a k_{\parallel} value near the \bar{K} point of the 1×1 surface Brillouin zone (SBZ) for surface state a . The two peaks labeled a and a' are due to the Si-H and Si-Si backbond states, respectively, as has already been concluded in earlier experimental and theoretical studies. The surface-state bands obtained by Pandey¹ using tight-binding calculations of the monohydride H/Si(111) 1×1 surface showed two surface states located at -5.02 and -3.88 eV relative to the VBM at the \bar{K} point. In our spectrum, these surface states are found at -5.50 and -4.50 eV relative to the Fermi level. The peak labeled b corresponds to the structure discussed as a surface resonance by Gallego *et al.*³ The widths of the a and a' features have been used to assess the quality of the 1×1 surfaces produced by the two main techniques, i.e., exposure to atomic hydrogen *in situ* or *ex situ* chemical etching.⁷ The widths of a and a' are 250 and 175 meV in Fig. 2(a), respectively. These values are significantly smaller than those reported in Ref. 7 (330 and 280 meV), which indicates that our surface is as well ordered as the ones prepared by chemical etching. Figure 2(b) shows a spectrum of the H/Ge(111) 1×1 surface obtained along the $\bar{\Gamma}-\bar{K}-\bar{M}$ azimuth at an emission angle of 36° , probing the surface state a near the \bar{K} point. Similar features as those in the spectrum from H/Si(111) 1×1 are observed, namely a , a' , and b . In the theoretical calculations performed by Pandey,¹ the energy positions of the surface states a and a' were determined. At the \bar{K} point they are located at -4.70 and -3.77 eV relative to the VBM, respectively. In our

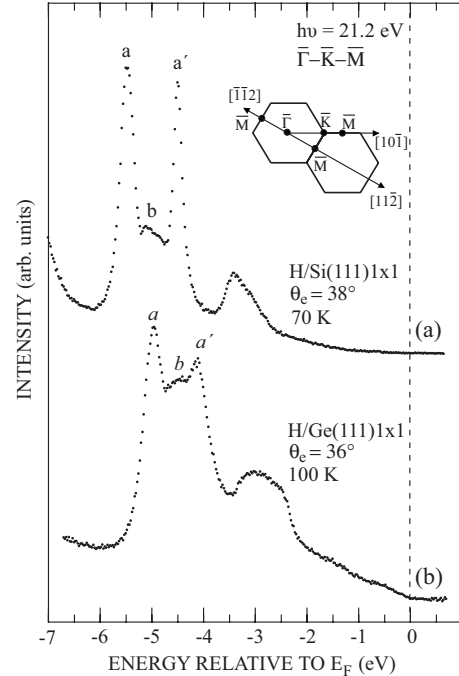


FIG. 2. Angle-resolved photoelectron spectra obtained from (a) the H/Si(111) 1×1 surface probed along the $\bar{\Gamma}-\bar{K}-\bar{M}$ azimuth at an emission angle of 38° and from (b) the H/Ge(111) 1×1 surface probed along the $\bar{\Gamma}-\bar{K}-\bar{M}$ azimuth at an emission angle of 36° . These emission angles correspond to k_{\parallel} values near the \bar{K} point of the 1×1 SBZs for the a and a' surface states of Si(111) and Ge(111), respectively. Both spectra were recorded at low temperature using a photon energy of 21.2 eV.

spectrum in Fig. 2(b), they are found at ~ -4.93 and ~ -4.15 eV relative to the Fermi level. Also the H/Ge(111) 1×1 surface exhibits a peak, b , between peaks a and a' . In this work, however, we do not have enough experimental data to discuss the surface resonance character of this structure as was done in Ref. 3.

The valence-band structure of the H/Ge(111) 1×1 surface was studied in detail by ARPES. Spectra were recorded along the $[10\bar{1}]$ azimuthal direction corresponding to the $\bar{\Gamma}-\bar{K}-\bar{M}$ line in the 1×1 SBZ and along $[\bar{1}\bar{1}\bar{2}]$ and $[11\bar{2}]$ corresponding to the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ line. All spectra were recorded at 100 K. Figure 3 shows the energy positions as function of k_{\parallel} of features in the photoemission spectra obtained along the $[10\bar{1}]$ azimuth, using a photon energy of 21.2 eV. The figure contains information from 35 spectra covering the emission angle range from 0 to 85° . The circles correspond to data points obtained by manually determining the energy positions of the various peaks in the ARPES spectra and then calculating the binding energy vs k_{\parallel} dispersions. The superimposed colored dispersion curves, represent a color coding of the second derivative obtained for each spectrum. The colors from yellow to black represent an increase in value of the second derivative. This procedure is known to reproduce the peak positions in the spectra and the intensity/sharpness of a structure is indicated by the darkness of the color scale. For instance, the peaks a and a' in Fig. 2(b) are

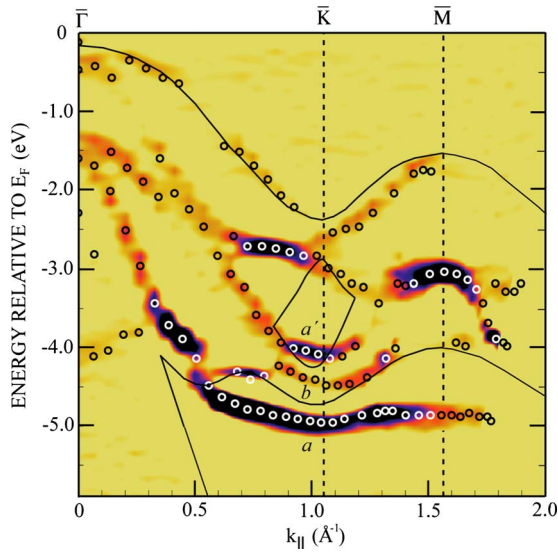


FIG. 3. (Color online) Energy vs k_{\parallel} dispersions of the features in the photoemission spectra measured with 21.2 eV photons along the $[10\bar{1}]$ azimuth. The circles correspond to manually determined peak positions in the ARPES spectra while the colored dispersions were computer generated as described in the text. The solid lines show the edges of the projected bulk band structure from Ref. 12.

represented by black and dark blue colors at the \bar{K} point in Fig. 3 while structure b is represented by a yellow color. To facilitate the distinction between bulk related dispersions and surface-state bands, the edges of the projected bulk band structure from Hata *et al.*¹² are also included. An energy separation of 0.17 eV between the Fermi level and the VBM has been determined by Guichar *et al.*¹³ for clean Ge(111) $c(2\times 8)$. Since we did not notice any shift of the spectra due to the hydrogen adsorption we have used the 0.17 eV value for the difference between the VBM and the Fermi level in Fig. 3. Four steep dispersion curves start out from the $\bar{\Gamma}$ point, two at ~ -0.4 eV and two at ~ -1.5 eV. Some of the dispersions overlapping the projected bulk bands originate from direct bulk transitions as discussed in Refs. 8, 14, and 15. We will not try to make a detailed identification of these dispersions, instead we concentrate on the hydrogen-induced structures a and a' and the structure b in between.

At the \bar{K} point, interesting features are observed. The band labeled a' is located at around -4.15 eV; i.e., it is located inside the band-gap pocket and is therefore a true surface state. This state has been identified in the case of H/Si(111) 1×1 as due to backbonds between first and second layer atoms of the substrate. The backbond state is only strong for k_{\parallel} values close to \bar{K} . However, the continuous dispersion curve indicates that the backbond state can be followed as a surface resonance for smaller k_{\parallel} values. This picture is consistent with the character of the corresponding Si-Si backbond state first observed on H/Si(111) 1×1 by Landmark *et al.*² The Ge-H surface state, a , is located in the lower band-gap pocket, and the dispersion can be followed up to the \bar{M} point. The structure b disperses inside the

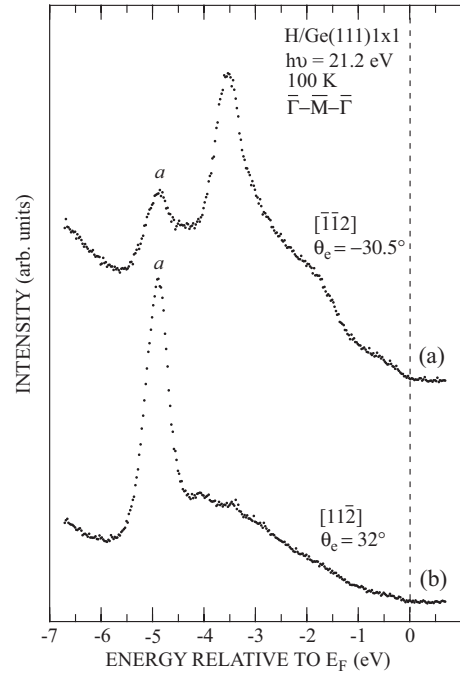


FIG. 4. Angle-resolved photoelectron spectra obtained from the H/Ge(111) 1×1 surface probed along the $[1\bar{1}\bar{2}]$ and $[\bar{1}\bar{1}\bar{2}]$ directions by using positive and negative emission angles, respectively. Both spectra probe the state, a , close to the \bar{M} point.

narrow channel in the projected bulk band structure as is also the case for H/Si(111) 1×1 . The dispersion follows closely those identified as due to direct transitions in other studies.^{8,14}

Figure 4 shows valence-band spectra of the H/Ge(111) 1×1 surface along the $[1\bar{1}\bar{2}]$ and the $[\bar{1}\bar{1}\bar{2}]$ azimuths obtained with a photon energy of 21.2 eV at 100 K. The emission angles, 32 and -30.5° , are selected such that they correspond to the k_{\parallel} values close to the \bar{M} point of the 1×1 SBZ. Both spectra showed the presence of peak a , which is attributed to the Ge-H surface state. This surface state is located at

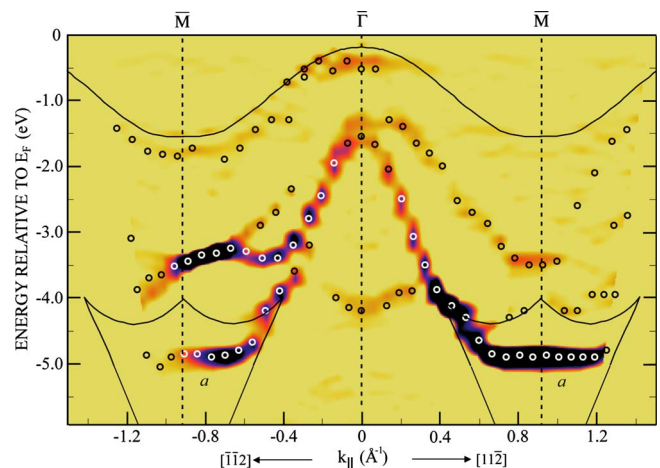


FIG. 5. (Color online) Energy vs k_{\parallel} dispersions of features in the photoemission spectra measured with 21.2 eV photons along the $[11\bar{2}]$ and $[\bar{1}\bar{1}\bar{2}]$ azimuths.

~ -4.9 eV at the \bar{M} -point in both the $[11\bar{2}]$ and $[\bar{1}\bar{1}2]$ directions. The strong peak at ~ -3.5 eV in the $[\bar{1}\bar{1}2]$ spectrum originates from a direct bulk transition.

Figure 5 shows the energy dispersions of features in the photoemission spectra obtained along the $[11\bar{2}]$ and $[\bar{1}\bar{1}2]$ azimuths. The highly dispersive structures account for the direct bulk transitions in agreement with previous studies.^{14,15} The hydrogen-induced surface band, a , appears inside the band-gap pocket in the vicinity of the \bar{M} point in both directions. Since there is no upper band-gap pocket in these azimuths there is no basis for finding surface state a' here.

In summary, the electronic structure of the H/Ge(111) 1×1 surface was investigated using angle-resolved photoelectron spectroscopy. The band structures of two surface states arising from the Ge-H bonds (a) and the Ge-Ge backbonds

(a') were determined. In the $\bar{\Gamma}-\bar{K}-\bar{M}$ azimuth, a and a' are located within the lower and upper band-gap pockets, respectively. In the $\bar{\Gamma}-\bar{M}$ direction, only the Ge-H state, a , can be observed. It appears as a very strong peak in the band-gap pocket around the \bar{M} point in the $[11\bar{2}]$ azimuth, while it is significantly weaker in the $[\bar{1}\bar{1}2]$ azimuth. The difference in the intensities is likely to be a consequence of the experimental geometry. The dispersion of structure b follows what is expected for spectral features due to direct transitions. To determine if b has some surface resonance character, as has been reported for a similar structure on H/Si(111) 1×1 , requires some further investigations.

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