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Electronic passivation of Si(111) by Ga–Se half-sheet termination

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A Si(111):GaSe van der Waals surface is prepared using sequential deposition of Ga and Se at elevated temperature on a Si(111)- 7×7 surface. Surface properties were investigated by soft x-ray photoelectron spectroscopy and low-energy electron diffraction. The Si(111)- 1×1 :GaSe surface remains with electronic surface potentials near flatband condition. © 2002 American Institute of Physics. [DOI: 10.1063/1.1454228]

Silicon is the most frequently used substrate material for many semiconductor applications in optoelectronic devices and sensor functions. A disadvantage of silicon is the high density of surface and interface states, which leads to high charge carrier recombination velocities. Electronic passivation of these states is important for many applications. Electronic passivation of semiconductor surfaces requires electronic states which are situated outside the fundamental Si band gap (see Ref. 1 and references therein). Saturation of dangling bonds at Si(111) is possible, e.g., by hydrogen or arsenic. Tight binding surface molecule calculations suggest the bonding and antibonding Si–H states to be at 8.96 eV below and 4.67 eV above the valence band maximum, respectively.¹ More detailed first-principles quasiparticle calculations agree with angle-resolved band structure determinations showing occupied surface states well below the valence band edge.^{2,3} A strong reduction of surface state density by hydrogen termination has also been shown by electric measurements.⁴ In addition to the bonding and antibonding electronic states of the Si-adsorbate bond at the Si:H surface, there is a doubly occupied lone pair orbital at the Si(111):As surface, with an energy well below the valence band maximum.⁵ The lone pair orbital therefore does not impede electronic passivation.

Epitaxial growth involving van der Waals surfaces was first utilized by Koma⁶ and subsequently examined by different research groups (see Ref. 7 and references therein). The heterostructure GaSe on Si(111) is one of the best studied systems in this context.^{8–11} The interface develops by forming a chemically saturated Si(111):GaSe surface,^{8,9} which is also chemically very stable.¹⁰ In addition, surface terminations of Si(110) and Si(100) with GaSe have also been investigated.¹¹

In this contribution we report on the electronic passivation of the Ga–Se terminated Si(111) surface, which is studied by photoelectron spectroscopy and low-energy electron diffraction (LEED). The structure of this surface is characterized by a layer of Ga between the topmost Si atoms and an outermost Se layer^{8,9} (see also Fig. 1). Each Si atom bounds to one Ga atom and to three Si back bonds, while each Ga

has one Si and three Se bonding partners. Each Se atom binds to three Ga atoms and has a doubly occupied lone pair frontier orbital. The Ga–Se surface layer has a structure which is identical to a Se–Ga–Ga–Se unit layer of GaSe single crystals cut between the Ga–Ga bond. An isolated half-sheet of GaSe has a hexagonal array of singly occupied Ga dangling bond orbitals with a lattice constant of 3.74 Å, which matches closely to a bulk Si(111) plane. Therefore a Ga–Se half-sheet termination layer should provide an ideal passivation for Si(111) surfaces, which is expected to be stable also as a substrate for subsequent layer growth.

Our experiments were performed with a multitechnique surface analysis system. Gallium and selenium deposition was done in an attached homemade MBE chamber. All chambers have a base pressure of better than 2×10^{-9} mbar. Different procedures have been reported for preparation of a Si(111):GaSe surface termination. These are depositions of GaSe onto either hydrogen terminated silicon surfaces⁸ or onto a Si(111)- 7×7 surface⁹ at temperatures which prevent the growth of epitaxial GaSe layers ($>500^\circ\text{C}$). It is also possible to selenize a monolayer of Ga,

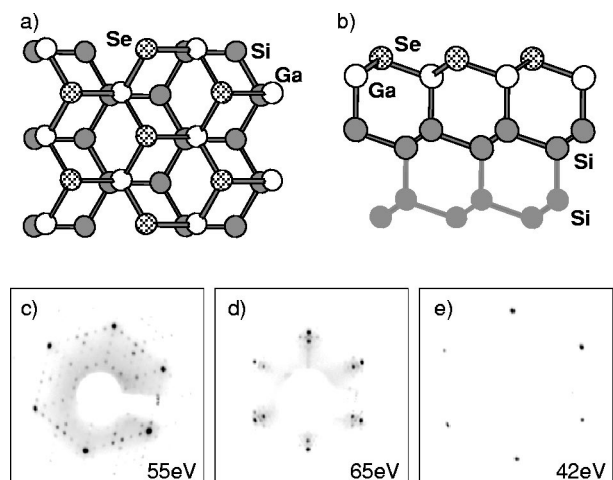


FIG. 1. Atomic arrangement of Si(111):GaSe surface termination in top (a) and side (b) view. The perspective in (a) is slightly tilted from [111]. LEED patterns of Si(111) during surface passivation: (c) Si(111)- 7×7 , (d) Si(111)- $6.3\sqrt{3}\times 6.3\sqrt{3}$:Ga, and (e) Si(111)- 1×1 :GaSe. Kinetic energies are indicated.

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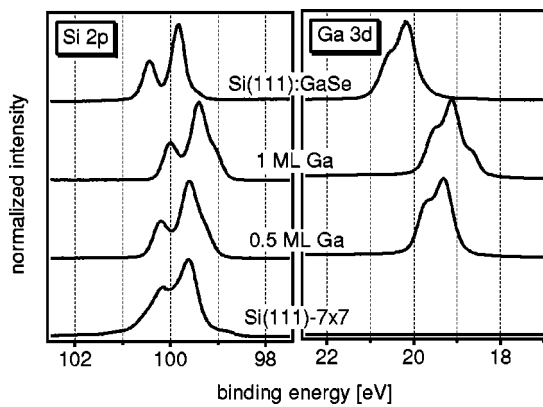


FIG. 2. Si $2p$ and Ga $3d$ core-level spectra of n -Si(111) during surface passivation: Spectra for 1 monolayer (ML) Ga coverage correspond to $6.3\sqrt{3} \times 6.3\sqrt{3}$ reconstruction. Excitation energy is $h\nu = 140$ eV.

which has been deposited on Si(111)- 7×7 at elevated temperatures.⁹ We have adopted the latter procedure as it is possible to follow the evolution of charge transfer between Si and the surface layer.

In Fig. 1(c) the diffraction pattern obtained after flashing an electrochemically hydrogen terminated n -type Si sample at 1000°C is shown. Figure 1(d) corresponds to a $6.3\sqrt{3} \times 6.3\sqrt{3} - R30^\circ$ reconstruction, which is reported for monolayer coverages of Ga deposited at about 550°C .¹² After selenization a threefold 1×1 LEED pattern [Fig. 1(e)] is obtained, identifying the chemical passivation of the silicon dangling bonds by a GaSe termination layer.^{8–11}

Photoelectron spectra were recorded with $h\nu = 140$ eV photons supplied by the U49-2/PGM2 beamline of the BESSY II storage ring in Berlin. Binding energies were calibrated using a gold foil and determined by a least-squares analysis employing Voigt profiles. The binding energy of the Au $4f_{7/2}$ level with respect to the Au Fermi edge is determined as $E_B = 83.94$ eV. Si $2p$ and Ga $3d$ core-level spectra as obtained for different surface conditions are shown in Fig. 2. The shape of the Si $2p$ level for Si(111)- 7×7 (Fig. 2) is somewhat less resolved but otherwise agrees with published data.¹³ We determine a binding energy of $E_B = 99.63$ eV for the Si $2p_{3/2}$ bulk component with respect to the Au Fermi edge. With the reported energy difference between the Si $2p_{3/2}$ level and the valence band maximum of $E_B(\text{Si } 2p_{3/2}) - E_V = 98.74$ eV (Ref. 14) this would correspond to a surface Fermi level position of $E_F - E_V \approx 0.89$ eV. In contrast a value of $E_F - E_V = 0.63$ eV is reported for the 7×7 surface.¹⁴ We attribute this deviation to differences in absolute binding energy determination, rather than to surface preparation or to experimental artifacts. Surface photovoltages, e.g., which can be induced by the high intensity synchrotron source,¹⁵ can be excluded since we have found identical binding energies for 7×7 surfaces prepared on n - and p -type substrates. As the relative binding energies are generally more accurate we take $E_B(\text{Si } 2p_{3/2}) - E_V = 99.00$ eV.

At approximately half monolayer Ga coverage (Fig. 2) the binding energy of the Si $2p$ bulk component is not changed. However, the characteristic shape for the Si(111)- 7×7 surface disappears and is replaced by a two component emission structure with a high intensity bulk

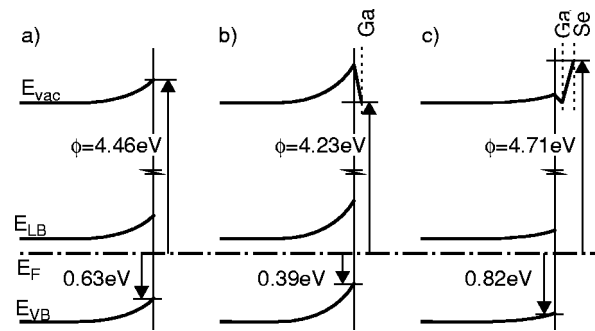


FIG. 3. Surface energy band diagrams for Si(111)- 7×7 (a), Si(111):Ga (b), and Si(111):GaSe (c).

emission and a low intensity shoulder at lower binding energy (Fig. 2). For monolayer Ga coverage a shift of 240 meV to lower binding energy is observed, due to an increase of band bending in the n -doped substrate. With $E_B(\text{Si } 2p_{3/2}) - E_V = 99.00$ eV this corresponds to a surface Fermi level position of $E_F - E_V = 0.39$ eV, in good agreement with the value of 0.35 eV given by Althainz *et al.* for the Ga/ p -Si(113) Schottky barrier height.¹⁶

The Ga $3d$ core level emission shows only a single component up to a coverage of half a monolayer (Fig. 2). With further deposition the shape changes and a second Ga component appears (Fig. 2). This second component has also been observed by Althainz *et al.*¹⁶ for a coverage approaching one monolayer and can be attributed to excess atoms situated on top of the first monolayer Ga. In addition a ~ 200 meV shift to lower binding energy is observed for the main Ga $3d$ component between half and one monolayer coverage, which is also observed for the Si $2p$ level and therefore attributed to the increase of band bending in the Si substrate.

Photoelectron spectra as obtained after selenization of the Ga film are shown in Fig. 2. The Ga $3d$ line is symmetric with a single component and is shifted to higher binding energy due to substrate band bending and chemical shifts. A well resolved single component at $E_B = 55.0$ eV is observed for the Se $3d$ emission line (not shown). The spectral shape of the Si $2p$ core level is dominated by a single component, corresponding to the bulk Si emission in agreement with spectra published recently.⁹ A small additional component can also be identified at lower binding energy. This is most likely attributed to an incomplete passivation of the (111) surface as a result of the preparation procedure. The Si $2p$ bulk component is shifted to a binding energy of $E_B = 99.82$ eV, which corresponds to a surface Fermi level position of $E_F - E_V = 0.82$ eV. Almost flatband condition at the surface of the n -type silicon sample is therefore achieved. The energetic situation of the surface after the different preparation steps is summarized in Fig. 3, where we have included work functions of the sample, which were determined from the secondary electron cutoff of HeI excited ultraviolet photoelectron spectra.

Obviously nearly flatband conditions can be achieved at the (111) surface of n -type silicon by the van der Waals termination with a GaSe half sheet. There is further evidence that the GaSe surface termination leads to an electronic passivation of the Si(111) surface. Angle-resolved valence band photoemission spectroscopy has been performed to deter-

mine the surface band structure.¹⁷ The electronic structure of the surface can be described by an almost undisturbed GaSe band structure, where the Ga–Ga bond is replaced by the Si–Ga bond giving an almost one-to-one replacement of the corresponding energy levels. It is further observed that the dangling bond lone pair states are just below the Si valence band maximum. Since GaSe has a rather large band gap of $E_g = 2.03$ eV (Ref. 7) it can therefore be anticipated from the electronic structure determination that no electronic states of the Si(111):GaSe half-sheet termination layer are located within the Si band gap in agreement to the results presented here. We have further performed experiments using *p*-type silicon samples. In this case it was so far not possible to achieve complete flatband conditions, most likely because of the imperfect preparation technique. However, for GaSe termination of *p*-type samples we have reached binding energies 0.5–0.6 eV lower than those for *n*-type silicon samples, indicating that the GaSe half-sheet termination layer is also able to passivate (111) surfaces of *p*-type Si samples.

Compared to other silicon surface terminations by hydrogen² or As (Ref. 5) the Si $2p$ level of the Si(111):GaSe surface shows no chemically shifted surface component within the experimental uncertainty (see Fig. 2 and Ref. 9). This indicates very small charge transfer between Si and Ga, or, in other words, a nonpolar chemical Si–Ga bond. The stepwise preparation of the Si(111):GaSe surface applied here has the advantage of following the evolution of charge transfer. With deposition of Ga the electron affinity (distance between conduction band minimum and vacuum energy) decreases as shown in Fig. 3(b). This indicates a surface dipole with its positive end towards vacuum or charge transfer from Ga to Si, in agreement with the larger electronegativity of Si. Selenization of the Si(111):Ga surface leads to a strong increase of the electron affinity [Fig. 3(b)]. The reversal of the surface dipole can be explained by charge transfer from Ga to Se, which is even more electronegative than Si. As the polarity of the Ga–Se bond leads to a strong charge transfer from Ga to Se, the positive charge at the Ga atom lowers the energy of the Ga frontier orbital.¹⁸ This explains that selenization almost eliminates the polarity of the Ga–Si bond, which is deduced from the absence of Si surface core-level shifts and from the similarity of the Ga–Ga to the Ga–Si electronic states found in the band structure determination.¹⁷

In summary it has been shown that the Si(111) surfaces can be electronically passivated by a GaSe half sheet, leading to a van der Waals surface. The bond between the Si surface

atom and the Ga atom of the half sheet is nonpolar and no charge transfer between Si and the half sheet occurs. In conjunction with the chemical inertness and temperature stability of the surface, which is superior to any other Si surface terminations, the GaSe termination generates an outstanding surface to be used for Si based heterostructure devices. We are planning to complement our results with surface recombination velocity measurements, which would allow to quantify electronic surface passivation.

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