

Chemical passivity of III-VI bilayer terminated Si(111)

Jonathan A. Adams^{a)} and Aaron A. Bostwick^{b)}*Department of Physics, University of Washington, Seattle, Washington 98195*

Fumio S. Ohuchi

Department of Materials Science and Engineering and Center for Nanotechnology, University of Washington, Seattle, Washington 98195

Marjorie A. Olmstead

Department of Physics and Center for Nanotechnology, University of Washington, Seattle, Washington 98195

(Received 17 June 2005; accepted 30 August 2005; published online 17 October 2005)

The chemical stability of Si(111), terminated with bilayer AlSe and GaSe, upon exposure to atmosphere, N₂ and O₂, was investigated with core-level and valence band photoelectron spectroscopy. Si(111):GaSe and Si(111):AlSe both form stable, unreconstructed surfaces with no states in the silicon energy gap; their atomic structures are nearly identical. However, similarities in surface electronic and atomic structure do not imply similar chemical passivity. While Si(111):GaSe is largely unaffected by the exposures, Si(111):AlSe reacts irreversibly with both pure O₂ and atmosphere, removing over $\frac{1}{3}$ of the Se and permanently destroying long-range order. © 2005 American Institute of Physics. [DOI: 10.1063/1.2112200]

Chemical and electronic passivation of silicon surfaces is of vital importance to micro- and nanoelectronics. Future device technologies will require integration of Si with spintronic, optoelectronic or organic materials without an intervening amorphous oxide layer. Of particular interest are passivation schemes that chemically saturate surface bonds without reconstructing the surface or introducing electronic states in the Si band gap.

Ideally-terminated Si(111) contains a single half-filled orbital per surface atom; this is unstable and the resulting four-layer deep, 7 × 7 reconstruction must be removed during heteroepitaxy. Addition of hydrogen saturates the dangling bond and removes the driving force for reconstruction, leading to a chemically passive, 1 × 1 surface with the now doubly-occupied orbital well-below the valence band maximum (VBM).^{1,2} Replacement of the top Si and H by arsenic, with five valence electrons, likewise leaves the surface passivated with a doubly-occupied lone-pair and three Si–As bonds.^{3,4} Replacing the topmost Si bilayer with GaSe^{5–9} or AlSe¹⁰ is isoelectronic to Si(111):H and Si(111):As—AlSe is equivalent to transferring a proton from Si to As at the Si(111):As surface.

These four isoelectronic surfaces all have no states in the Si energy gap; however, their differing thermal and chemical stability, as well as differing surface electronic dipoles, imply different potential uses. AlSe termination is stable to the highest temperature in ultrahigh vacuum (UHV), above 750 °C,¹¹ in contrast to 700 °C for Si(111):As,³ 600 °C for Si(111):GaSe,⁵ or 500 °C for Si(111):H.¹² Significant chemical passivity is reported for Si(111):H,¹³ Si(111):As,⁴ and Si(111):GaSe,^{14,15} but there are no previous reports for AlSe termination. In this letter we investigate the relative chemical stability of GaSe and AlSe bilayer terminations of Si(111) with core-level and valence band photoelectron spectroscopy. In contrast to As, H, or GaSe termination, Si(111):AlSe is not stable under exposure to O₂ or atmosphere, despite the

extreme similarity of the atomic and electronic structure between Si(111):GaSe^{6,16} and Si(111):AlSe.¹⁰

GaSe and AlSe were deposited by molecular beam epitaxy from stoichiometric GaSe and Al₂Se₃ sources, respectively, onto Si(111)7 × 7. Substrates (*p*-type, $\rho \sim 1 \Omega \text{ cm}$) were prepared with a chemical oxide,¹⁷ and outgassed in UHV at $\sim 650 \text{ }^\circ\text{C}$ for $\geq 12 \text{ h}$ before removing the oxide by repeated 5–10 s anneals to $\sim 1000 \text{ }^\circ\text{C}$ until a well-ordered 7 × 7 LEED pattern was observed. Samples were heated by direct current; the temperature was monitored using an optical pyrometer. Sample cleanliness was checked by x-ray photoelectron spectroscopy.

Growth conditions were chosen to self-limit at a single bilayer ($T_{\text{sub}} = 540 \text{ }^\circ\text{C}$ and flux = 6 Å/min for GaSe; $T_{\text{sub}} = 660 \text{ }^\circ\text{C}$ and flux = 4.5 Å/min for AlSe).^{5,10,11} Substrates were exposed to the flux for 3 min, followed by 30–60 s at the growth temperature without flux. Samples were transferred under UHV from the MBE growth chamber to the analysis chamber (base pressure 3×10^{-10} Torr).

Sample exposures were carried out in a load lock chamber with base pressure 1×10^{-7} Torr. Exposure gases O₂ and N₂ were leaked from bottled sources (99.95% and 99.99% purity, respectively), undissociated, until the load lock pressure reached $\sim 1 \text{ atm}$. Ambient air was leaked in for atmospheric exposure. Samples were exposed for 10 min at room temperature; the load lock was then pumped out with a turbomolecular pump and the sample transferred back to the analysis chamber. A Mg K_α x-ray source ($h\nu = 1253.6 \text{ eV}$) was used for core-level spectra and a 21.2 eV He I discharge lamp for valence-band photoemission.

The effect of atmospheric exposure on core-level spectra (CLS) for GaSe and AlSe-terminated Si(111) is shown in Fig. 1. For GaSe, the Ga, Se, and Si CLS are unaffected by exposure to atmosphere except for a small decrease in intensity and in work function: the relative CL binding energies and the peak widths are unchanged, and there are no secondary components identifiable within our experimental resolution. Exposure of Si(111):GaSe to N₂ and O₂ showed similar results, though with slightly different Fermi level (E_F) posi-

^{a)}Present address: Advanced Portfolio Technologies, Ltd., London.^{b)}Present address: Advanced Light Source, Berkeley, California.

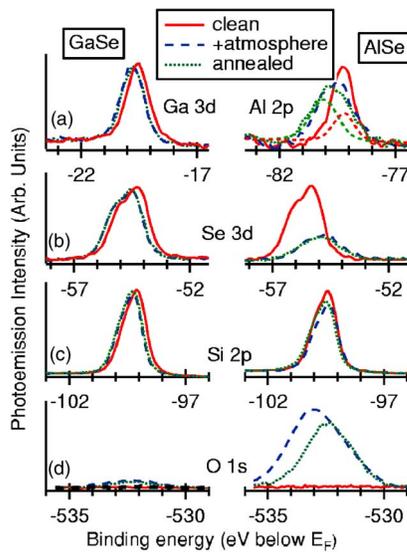


FIG. 1. (Color online) Effect of atmospheric exposure on core-level emission. Mg $K\alpha$ ($h\nu=1253.6$ eV) excited emission for GaSe (left) and AlSe (right) terminated Si(111) before (solid line) and after (dashed line) exposure to atmosphere and a subsequent anneal (dotted line). (a) Ga $3d$ (left) and Al $2p$ (right); (b) Se $3d$; (c) Si $2p$; (d) O $1s$. Short-dashed lines in (a) are least-square fitted components for post-anneal Al $2p$. Dark dashed line in (d) is O $1s$ emission after atmospheric exposure of a GaSe-terminated surface grown with excess Se.

tions relative to the bands (see Fig. 2), as did exposure to CO_2 or to N_2 saturated with H_2O (data not shown).

The slight changes in CLS upon exposure of Si(111):GaSe likely results from physisorbed gases. For the samples in Fig. 1, ~ 2 ML carbon¹⁸ and 0.2 ML oxygen adsorbed during atmospheric exposure; all C was removed by annealing the sample to 480 °C for 1 min. Approximately 0.2 ML O accumulation was also observed after O_2 exposure, but no C was detected; no added N, C, or O was observed after N_2 or CO_2 exposure. The O accumulation during atmospheric exposure varies with sample preparation. The dark dashed line in Fig. 1(d) shows no detectable O accumulation upon atmospheric exposure of a sample prepared with a combined Se electrochemical source and stoichiometric GaSe Knudsen source. Scanning tunneling microscopy of Si(111):GaSe reveals occasional Ga-terminated regions,¹⁹ which are likely locations for O reactivity that would be eliminated with excess Se. Photoemission measurements on similarly prepared surfaces show this preparation greatly reduces the metallic Ga concentration on the surface.²⁰

In contrast to Si(111)GaSe, Si(111):AlSe shows dramatic changes upon atmospheric exposure. Fig. 1(a) shows significant broadening of the Al $2p$ spectrum upon exposure, although the total peak areas are comparable. The short-dashed lines in Fig. 1 denote the two components in a least-squares fit to the Al $2p$ spectrum after atmospheric exposure and a 450 °C, 1 min anneal. About 40% of the total intensity remains in a peak at the position of the original uncovered bilayer, while the remainder is in a broad peak shifted ~ 0.7 eV to higher binding energy (HBE).

In Fig. 1(b), the post-exposure Se $3d$ core-level shows $\sim 60\%$ reduction in total intensity, comparable to the fractional decrease in the Al $2p$ bilayer component. The Se $3d$ has broadened, but any distinct components are hidden by the large (0.85 eV) Se $3d$ spin-orbit splitting. The Si $2p$ emission, Fig. 1(c), is reduced in intensity by $\sim 10\%$ with

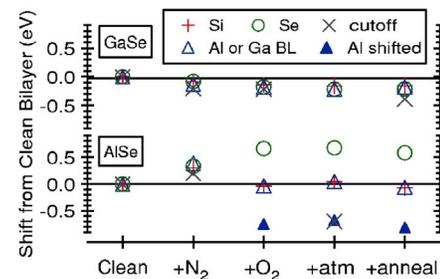


FIG. 2. (Color online) Shift in electron kinetic energy for core-level photoemission and low-energy cut-off of the secondary emission as a function of sample treatment for GaSe (top) and AlSe (bottom) terminated Si(111). A positive shift in kinetic energy reflects a lower CL binding energy.

exposure; there is no clear SiO_x peak, indicating O is confined to the surface layer(s).

The O $1s$ core-level [Fig. 1(d)] shows a significant amount of O present after exposure. Using calculated relative cross sections²¹ of O, Al, and Se, and assuming 1 ML for the pre-exposure Al and Se coverage, the O accumulation is ~ 4 ML. About $\frac{1}{4}$ of this is removed by a 450 °C, 1 min anneal, primarily from the high binding energy side of the original peak. About 1 ML C accumulated during atmospheric exposure, all of which disappeared with the anneal. The Al $2p$, Se $3d$ and Si $2p$ emissions were essentially unchanged by the anneal except for a small (~ 0.1 eV) shift to HBE.

Exposure of Si(111):AlSe to N_2 showed no accumulation of N, O, or C, nor noticeable changes in lineshape for the Al, Se, or Si peaks. Exposure to O_2 , on the other hand, was similar to atmospheric exposure except for the absence of carbon. The Al $2p$ again broadens with roughly constant total peak area, while the Se $3d$ peak decreases by more than a third and broadens significantly. The total O accumulation is again about 4 ML, with ~ 3 ML remaining after a 450 °C anneal.

Kinetic energy shifts in CL peak positions as a function of sample treatment are shown in Fig. 2. The shift in the low-energy cutoff of the Mg $K\alpha$ secondary emission is also shown, measured in normal emission by biasing the sample to +15.0 V; a positive value in Fig. 2 reflects an increase in sample work function $\Phi = E_{\text{vac}} - E_F$. For GaSe, no change in chemical environment is apparent. All three emission peaks and the low-energy cutoff exhibit the same small shift to lower kinetic energy (HBE) upon exposure, indicating an overall decrease in Φ . It takes very few states on these passivated surfaces to shift the bands relative to the Fermi level from their initial \sim flat-band condition ($E_F - E_{\text{VBM}} = 0.15$ eV, p -type sample). The shift towards mid-gap is likely from addition or removal of surface adsorbates. The slightly larger shift of the low-energy cut-off than the CLS upon annealing may indicate an adsorbed surface dipole, but this exhibits sample-to-sample variations.

For Si(111):AlSe, only for N_2 exposure do the substrate and overlayer emission peaks, plus the low-energy cutoff, all exhibit the same shift; in this case the shift is to higher kinetic energy (lower binding energy, LBE), indicating an increase in Φ . However, the original Fermi level position was \sim mid-gap ($E_F - E_{\text{VBM}} = 0.45$ eV) and N_2 exposure flattened the bands, perhaps by displacing another contaminant. Both the O_2 and air exposures induce a chemical change in the surface. The Se $3d$ centroid moves to LBE, while the Si is close to its original (mid-gap) position. One of the Al com-

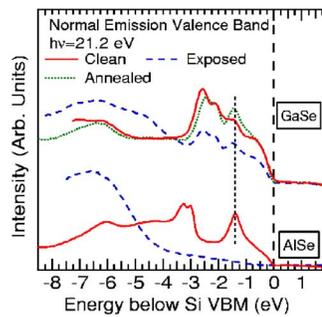


FIG. 3. (Color online) Normal emission valence band spectra excited by He I ($h\nu=21.2$ eV) photons for Si(111):GaSe (top) and Si(111):AlSe (bottom), before and after exposure to atmosphere. Spectra are aligned relative to Si valence band maximum (VBM) via the bulk Si emission 1.4 eV below the VBM (dashed lines).

ponents (open triangles in Fig. 2) maintains the same position relative to the Si 2p as the original bilayer peak, while a second Al component appears at HBE (closed triangles); the low-energy cutoff moves with this peak, indicating the reaction changes the surface dipole above the Si–Al bond. Annealing (600 °C for 30 s) simply shifts each peak slightly to lower kinetic energy, slightly changing the E_F position in the Si gap.

Figure 3 compares normal emission ($k_{\parallel}=0$) valence band spectra from Si(111):GaSe and Si(111):AlSe before and after atmospheric exposure. Clean Si(111):GaSe and Si(111):AlSe both exhibit several well-defined states associated with the Se lone pair, the (Al,Ga)–Se p_{xy} bonding orbitals, and the underlying bulk Si.^{10,16} After exposure, both surfaces exhibit a large, broad O 2p-derived peak at $E_B \sim 6-7$ eV, masking the sharper Al–Si or Ga–Si bonding state near the same energy. The GaSe/Si valence band is not otherwise altered by exposure; the full $E(k_{\parallel})$ band structure is unchanged (data not shown). Even the Se lone-pair state (shoulder, $E_B \sim -0.6$ eV), the most susceptible to changes in chemical environment, is not affected by atmosphere, unlike Si(111):As.⁴ This shows that long-range order on the surface is not impacted by the physisorbed gases, supporting the idea that any adsorption is at pre-existing defect sites. Annealing the sample returns the surface close to its initial condition. The AlSe bilayer is not as resilient: atmospheric exposure removes all recognizable states from the clean bilayer spectrum.

The atomic structures of Si(111):AlSe and Si(111):GaSe are nearly identical, with the Si–M and M–Se (M=Ga,Al) bond lengths the same to within 0.02 Å,^{6,10} the electronic structures are also similar.^{10,16} However, their chemical stabilities are very different. Si(111):GaSe is inert to the primary constituents of atmosphere as well as to laboratory air. Other researchers have reported Si(111):GaSe to be stable in O₂ up to 400 °C¹⁴ or in ambient air for up to 30 days.¹⁵ Si(111):AlSe, on the other hand, is not chemically stable. Not only is there a thermally stable accumulation of oxygen on the surface, but oxygen facilitates Se removal. A similar difference in reactivity with oxygen is reported for AlAs and GaAs,^{22–24} where AlAs oxidizes readily in air at room temperature while GaAs is stable up to 450 °C.

The chemically-shifted Al component and reduction in Se emission are consistent with an oxygen-selenium exchange reaction over $\sim 60\%$ of the surface. The constant lineshape the Si 2p emission indicates no more than

~ 0.5 ML of Si has reacted to form SiO_x. The suppression of the Si valence band states may indicate restructuring of the near-surface Si, although the reduction may also result from inelastic scattering through an amorphous oxyselenide overlayer.

In summary, the reactivity of GaSe and AlSe terminated Si(111) to atmosphere and its primary constituents was investigated. Both terminations are stable under exposure to undissociated N₂; Si(111):GaSe is chemically stable under all exposure conditions, with physisorbed contaminants removed by a mild anneal. Si(111):AlSe, while more thermally stable, readily oxidizes in air and O₂. Its high thermal stability would be advantageous in heteroepitaxy of materials that require a high temperature substrate, but the chemical reactivity would limit its use for growth of oxides. Finally, these results clearly demonstrate that structural and electronic similarities between surfaces do not necessarily indicate similarities in chemical reactivities.

This work was supported by NSF Grant Nos. DMR-0102427 and DMR-9801302. We thank T. Ohta for useful discussions. Portions were submitted by J.A.A. in partial fulfillment of the requirements for a Ph.D. in Physics at the University of Washington.¹¹

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