

Atomic Structure of Si(111):GaSe 1x1

S. Meng¹, A. Bostwick¹, B.R. Schroeder¹, E. Rotenberg², F.S. Ohuchi³, and M.A. Olmstead¹

¹Department of Physics, University of Washington, Seattle, Washington 98195 USA

²Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720 USA

³Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195 USA

INTRODUCTION

Epitaxy of III-VI materials (e.g. GaSe) on silicon is attracting increasing interest due to many distinct structural, electronic and optical properties displayed by chalcogenide-based semiconductors and their potential use in optoelectronic devices [1]. Under certain growth conditions, deposition of GaSe on Si(111)7x7 results in passivation of the surface by a single, unreconstructed GaSe bilayer.[2] The resultant Si(111):GaSe structure, with Si-Ga bonds and surface Se lone-pair states, is a fully coordinated surface, similar to Si(111):As. Additional GaSe does not stick to the bilayer at substrate temperatures above 525°C.

Si(111):GaSe is both the starting substrate for GaSe/Si heteroepitaxy and an interesting system in its own right. This passivated surface serves as a model system for initiation of binary-materials heteroepitaxy. The bilayer structure is the building block of two different bulk crystals: GaSe and Ga₂Se₃. It is amenable to theoretical calculations, providing tests of both photoelectron diffraction theory and of the impact of surface dipoles and charge rearrangement on structure.

We performed experiments to determine the Ga bonding site, and the Ga-Si and Ga-Se bond lengths and angles in the GaSe bilayer. Using scanned-energy photoelectron diffraction (PED), we determined that Ga resides 2.35Å above surface Si atoms, while the Ga-Se bond parameters are between those of the two bulk crystal structures. At kinetic energies near 200 eV, Ga PED is dominated by forward focussing along the three Ga-Se bonds, while Se PED displays diffraction rings from in-plane scattering. High resolution Si 2*p* spectra show interface Si to be in an extremely bulk-like environment, whereas angle-resolved valence emissions indicate GaSe has a long-range influence on the Si bands.

EXPERIMENTS

A GaSe bilayer was deposited from a stoichiometric GaSe source on Si(111)7x7 at 550°C. Photoelectron diffraction measurements were performed on a double rotating stage in the analysis chamber at ALS BL 7, which is connected to the deposition chamber by UHV transfer. The angle between the incident photons and detected electrons was fixed at 60° in the horizontal plane and the sample was rotated around the horizontal axis (θ) and the sample normal (ϕ).

RESULTS

(1) *k*-scan Photoelectron Diffraction. Our previous results determined that the bilayer has a single domain, with Ga in the lower atomic layer and Se in the upper layer [2]. The Ga-Si bonding configuration, inaccessible with high-energy PED, is crucial to the passivation process. To determine Ga bonding sites for the GaSe bilayer, we performed *k*-scan photoelectron diffraction measurements. Fig. 1a shows the measured Ga 3*d* photoelectron intensity modulation along the surface normal versus photoelectron wavenumber. The upper three curves correspond to

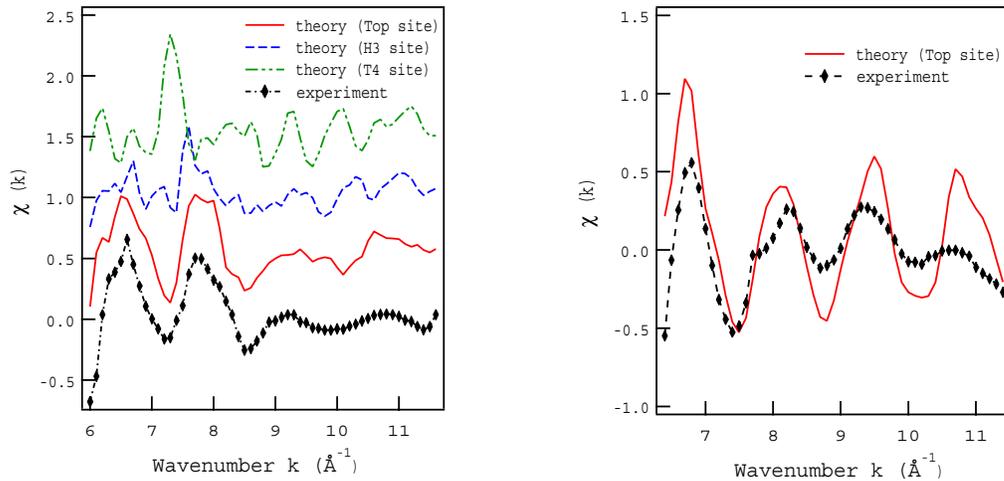


Figure 1. Intensity modulation versus photoelectron wavenumber in scanned-energy photoelectron diffraction. Left: Ga $3d$ PED along surface normal ($\theta = 0^\circ$, $\phi = 0^\circ$). The bottom curve shows experimental data. Upper three curves are theoretical calculations for Ga residing in top sites, H3 sites and T4 sites respectively. Right: Se $3d$ PED along Ga-Se bonding direction ($\theta = 64^\circ$, $\phi = 0^\circ$) and the corresponding theoretical calculation.

theoretical multiple-scattering calculation for bilayer structure with Ga above in the top (above 1st layer Si), H3 (above 4th layer) and T4 (above 2nd layer) site configurations, respectively. The best agreement is obtained for the configuration in which Ga sits directly atop surface Si. The observed intensity oscillations with wave number arise from interference between direct (unscattered) Ga emission and emission back-scattered from the underlying Si. Least square fitting gives Ga-Si bond length of 2.35\AA , equal to a bulk Si-Si bond. Fig 1b. shows a similar Se $3d$ k -scan PED measurement along the Ga-Se bond direction, which is about 64° from the surface normal. The solid line reflects the prediction using the bulk GaSe bond length.

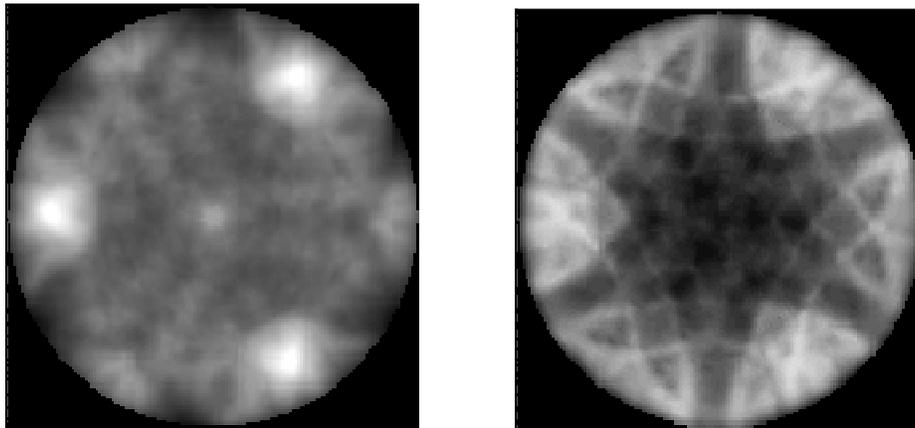


Figure 2. Stereographic projections of photoelectron intensity (holograms) from Si(111):GaSe at $h\nu=246$ eV. Left: Ga $3d$ (KE = 226 eV) PED hologram. Right: Se $3d$ (KE = 192 eV) PED hologram.

(2) Photoelectron Diffraction Holograms. Fig. 2 shows photoelectron diffraction holograms for Ga $3d$ and Se $3d$ core levels, taken at a photon energy of 246 eV. The holograms show the stereographic projection of photoelectron intensities as functions of both polar and azimuthal angles. The Ga $3d$ hologram exhibits strong diffraction spots along the three Ga-Se bonds, indicating forward focusing still dominates at this energy, though significant back-scattering can

also be observed along surface normal (see Fig. 1a). The three-fold symmetry confirms the existence of a single domain. The Se 3d hologram displays no strong diffraction features, indicating Se forms the top layer of the bilayer structure. The six-fold ripple pattern arises from scattering off the six in-plane Se next-nearest neighbors. The enhancement with three-fold symmetry near 64° arises from back-scattering off Ga nearest neighbors.

(3) Electronic Structure of the bilayer passivated surface.

GaSe bilayer terminated Si(111) bears a strong resemblance to As-terminated Si(111). In both cases, the resultant fully-coordinated surface contains a lone-pair state. We have measured the valence band structure of Si(111):GaSe with ARUPS and found that the uppermost state is indeed similar to that in Si(111):As [3]. However, the remaining bands are not closely reminiscent of Si(111):As. Rather, there is an unexpected splitting at the zone center and symmetry reflective of the surface rather than bulk Brillouin zone. We confirmed the surface character with normal emission, variable photon energy data acquired at the ALS. The GaSe bilayer thus affects the Si bands for an extensive distance, reflecting strain, surface dipoles, or some other long-range effect. However, core-level photoemission shows Si to be in an extremely bulk-like environment, as seen in Figure 3. No interface shift (<0.1 eV) of Si 2p was resolved, unlike the 0.75 eV shift of the Si(111):As system. This surprising result indicates that the core-level and valence bands can give “opposite” information on the bulk-like character of the near-surface Si.

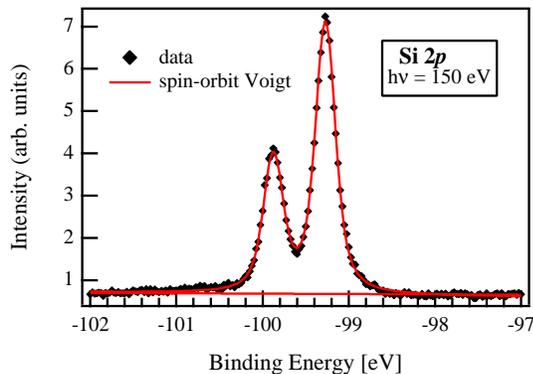


Figure 3. Surface sensitive Si 2p photoemission spectrum. Solid line indicates the fitted spin-orbit Voigt function.

ACKNOWLEDGMENTS

This work was supported by NSF grant DMR9801302 and DOE grant DE-FG03-97ER45646/A003. Experiments were performed at the Advanced Light Source of Lawrence Berkeley National Laboratory operated by DOE under Contract No. DE-AC03-76SF00098. We thank George Meigs for his expert technical assistance.

REFERENCES

1. F. S. Ohuchi and M. A. Olmstead, “Thin Film Growth of II-VI Compound Semiconductors,” Fumio S. Ohuchi and Marjorie A. Olmstead, *Encyclopedia of Electrical and Electronics Engineering*, John G. Webster, editor (John Wiley & Sons, New York, 1999).
2. S. Meng, B. R. Schroeder and M. A. Olmstead, *Phys. Rev. B* (to be published).
3. A. Bostwick, S. Meng, B. R. Schroeder, E. Rotenberg and M. A. Olmstead, in preparation.

Principal investigator: Marjorie Olmstead, Physics Department, University of Washington. Email: olmstead@phys.washington.edu. Telephone: 206-685-3031. Web: <http://faculty.washington.edu/olmstd>