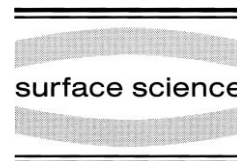




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Surface Science 442 (1999) L948–L952



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Surface Science Letters

## Structure of the Cl-passivated Ge(111) surface determined using X-ray absorption and first principles calculations

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Received 3 May 1999; accepted for publication 30 August 1999

### Abstract

Cl 1s (K shell) near-edge and extended X-ray absorption fine structure spectroscopy (EXAFS), and first-principles calculations have been used to quantify the Ge(111)–Cl surface structure. Cl passivation is achieved in ambient atmosphere by wet chemical methods. Strong polarization, observed both in the Cl 1s→3p  $\sigma$  resonance and in the extended fine structure region, proves that Cl forms a stable monochloride structure with Cl bonded to Ge in the atop position. A stable atop Cl–Ge monochloride structure was also found in our theoretical calculations. The calculated Ge(111)–Cl surface structure was used to refine the structural parameters by matching Feff calculations to the unfiltered experimental EXAFS signal. Excellent agreement between theory and experiment was found with the atop monochloride structure with a Ge–Cl bond length of  $2.17 \pm 0.01$  Å. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Ab initio quantum chemical methods and calculation; Germanium; SEXAFS; Surface structure

Clean semiconductor surfaces are highly reactive and thus surface oxide layers are readily formed upon exposure to air. These native surface oxides are very defective and generally undesirable in many applications such as epitaxial growth. Therefore surface passivation has been an active area of research [1–3]. Preparation of oxide-free surfaces which are air stable (for at least a few hours) is essential to many processes involved in epitaxial growth and device manufacturing [4,5]. Furthermore, well-ordered and air-stable semicon-

ductor surfaces provide a unique opportunity to integrate semiconductor and organic materials through molecular self-assembly [6,7]. One of us has discovered [8] that an air-stable Ge(111) surface can be obtained by Ge monochloride surface termination. This surface has been successfully used to grow alkyl films through molecular self-assembly [6]. Here we report a quantitative study of the Cl-passivated Ge(111) surface which combines X-ray absorption fine structure spectroscopy (XAFS) with first-principles structure calculation.

The experiments were carried out on the double-crystal (InSb) monochromator beam line at the Synchrotron Radiation Center (SRC) of the

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University of Wisconsin-Madison. The measurements were carried out in a vacuum chamber with a pressure in the low  $10^{-7}$  Torr range. The photon beam size was about  $1\text{ mm} \times 2\text{ mm}$ . The sample size was  $\sim 15\text{ mm} \times 30\text{ mm}$ . The photon incidence angle relative to the Ge(111) surface plane was  $20^\circ$ , fixed for all measurements. The sample holder can be rotated in one axis parallel to the photon incidence. For this work we measured the polarization dependence by recording spectra in two orientations:  $E_\perp$ , with the photon beam incident  $20^\circ$  off the surface plane but with the sample rotated so that the photoelectric vector  $E$  is approximately 'perpendicular' (i.e.  $70^\circ$ ) to the sample surface (111) plane, and  $E_\parallel$ , with the photon beam incident  $20^\circ$  off the surface plane but with the sample rotated so that the photoelectric vector is exactly parallel to the sample surface. The Ge(111) wafer was undoped and the surface was protected by a thin oxide film in epi-ready condition. The Cl chemical passivation involves immersion of the epi-ready sample in an aqueous hydrogen chloride solution ( $\text{HCl}(38\text{ wt.}\%):\text{H}_2\text{O}=1:1$ ) for 5 min followed by blow drying with nitrogen. After this treatment, the surface is found to be free of oxide, with a  $(1 \times 1)$  bulk-like structure, and with the surface terminated by Ge–Cl bonds, as established by measurements using X-ray photoelectron spectroscopy, low-energy electron diffraction, and Cl K near-edge structure [6].

The Cl 1s fluorescence signal was measured using a nine-element array of liquid nitrogen cooled, solid state Ge detectors. Fig. 1 shows the Cl 1s X-ray absorption spectra recorded with  $E_\perp$  and  $E_\parallel$  polarization. The spectra plotted are as-recorded data with a pre-edge linear background subtraction and edge-jump unit normalization. The sharp peak centered at  $\sim 2817\text{ eV}$  is the  $\sigma_{\text{Ge-Cl}}^*$  resonance, which is caused by photon-induced excitation of an electron in the Cl 1s level to the  $\sigma_{\text{Ge-Cl}}^*$  empty valence level. Transitions to p-like final states are favored because of angular momentum conservation. Fig. 1 shows that the  $\sigma$  resonance peak is strong in the  $E_\perp$  polarization and very weak, possibly absent in the  $E_\parallel$  polarization. This clearly indicates that the Cl–Ge bonding states,  $|\sigma_z\rangle$ , which are formed by the overlap of an atomic-like orbital  $|\text{Cl}, p_z\rangle$  and a surface

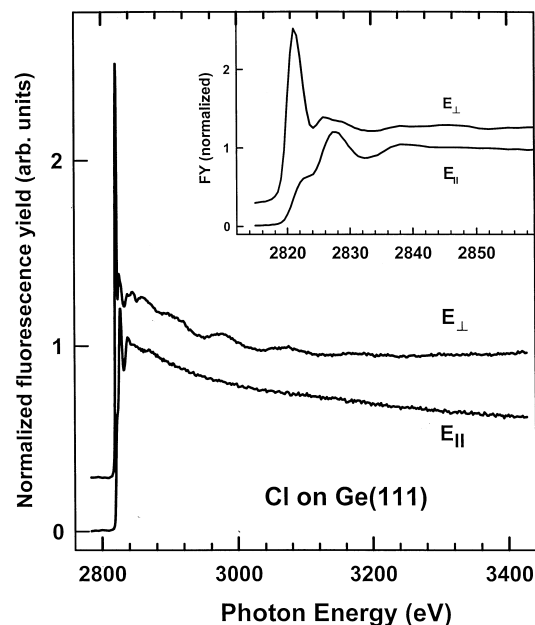


Fig. 1. Cl 1s X-ray absorption spectra in  $E_\perp$  and  $E_\parallel$  polarization of a Cl/Ge(111) surface prepared by wet chemical passivation. The near edge signal (XANES) is presented in more detail in the inset. The  $E_\perp$  signal has been offset for clarity.

dangling bond  $|\text{Ge}, sp^3\rangle$ , are aligned along the surface normal. The displacement in energy position of the second peak indicates a difference in the scattering paths to the XANES at these two extreme polarizations. This fluorescence yield experiment confirms previous near-edge results obtained using total electron yield detection [6]. The spectra shown in Fig. 1 are qualitatively similar to the spectra reported for Cl/Ge(111) prepared by exposing the reconstructed Ge(111) ( $2 \times 8$ ) surface to Cl gas under UHV conditions [9].

The Cl–Ge bond length was derived from analysis of the extended fine structure (EXAFS) signal. Fig. 2 compares the magnitudes of the Fourier transforms of the Cl 1s EXAFS signals obtained at the two different polarizations. The EXAFS signal was extracted from the  $E$ -space data shown in Fig. 1 by a three-section cubic spline background subtraction, with  $k=0$  set at the midpoint of the Cl 1s absorption jump for the  $E_\perp$  polarized spectrum. The magnitudes of the Fourier transforms (Fig. 2) are a phase-shifted, direction-

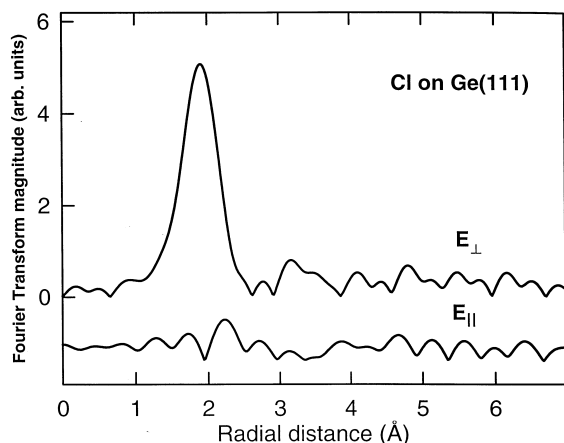


Fig. 2. Pseudo-radial distribution along the surface normal ( $E_{\perp}$ ) and in the surface ( $E_{\parallel}$ ) generated by the magnitude of the Fourier transform of the Cl 1s EXAFS spectra shown in Fig. 1.

ally dependent radial distribution about the Cl atom. The Fourier transform of the  $E_{\perp}$  data shows a strong first-shell signal at about 2 Å corresponding to backscattering from the Ge atom to which the Cl is bonded. In contrast to this, the transform of the  $E_{\parallel}$  data is essentially featureless. The dramatic difference in the EXAFS intensity in the two different polarization directions clearly indicates a strongly anisotropic local geometry. It shows that the first-shell neighboring atom to Cl is located along the surface normal, consistent with the conclusion drawn from the near-edge data.

Quantitative structural parameters (Cl–Ge bond length, coordination number, Debye–Waller factors) were derived using three approaches. First we carried out a single-shell analysis of the back-Fourier-filtered first-shell signal (1.1–2.5 Å) from the  $E_{\perp}$  EXAFS using tabulated Cl–Ge backscattering amplitudes and phase shifts based on Feff 3.0 calculations (Feff is the name of a computer software package [10]). This approach yields a Cl–Ge bond length of 2.20 Å and a polarization-corrected coordination number of 1.05. The Fourier transform of the  $E_{\parallel}$  data shows no backscattering atoms within the first shell. The second approach was based on matching the unfiltered  $k$ -space EXAFS signal to a more sophisticated Feff 6.01 [11] simulation of that signal which was derived from a fine tuning of the structure gener-

ated by geometry optimization using a high level quantum calculation. In the third approach we fit the experimental data in  $R$  space to the Feff 6.01 calculation of the first shell scattering. The fit gives a Cl–Ge distance of  $2.180 \pm 0.005$  Å, a Debye temperature of  $365 \pm 33$  K and  $E_0 = 3.2$  eV, the  $k$ -space origin (shift relative to the originally assigned  $k=0$  point, the inflection point on the  $E_{\perp}$  spectrum). When  $E_0$  was kept at 0 eV the distance was  $2.161 \pm 0.007$  Å. As a final value we report the average of these two evaluations, namely,  $2.17 \pm 0.01$  Å.

A first-principles determination of the structure of the Cl-terminated Ge-(111) surface was carried out using total energy minimization based on density functional methods [12], essentially as in Ref. [13]. We used the local-density approximation (LDA) and nonlocal, norm-conserving pseudo-potentials [14]. The Cl-terminated Ge crystal with a (111) surface was modeled by a slab of ten atomic layers of Ge, an eleventh layer of Cl, and five ‘empty’ layers to represent the vacuum. The first four layers had Ge atoms in their respective bulk positions and they were held fixed during the structure optimization to represent the ‘bulk’ of the crystal. The very first (‘bottom’) layer was saturated by four hydrogen atoms. The resulting system of 17 layers (including the vacuum region) was made periodic in the  $z$  direction, which is the  $\langle 111 \rangle$  direction. The surface unit cell was periodic in the  $x$ – $y$  plane. The  $x$  direction, i.e. [110], repeat distance was  $a_0\sqrt{2}$ , where  $a_0$  is the Ge lattice constant of 5.658 Å. The  $y$  direction repeat distance is  $a_0\sqrt{3}/2$ . Together these dimensions defined a rectangular surface unit cell with four atoms in each layer. A set of plane-wave states with a 10 Rydberg cut-off was used as the basis set for expanding the wavefunctions. Calculations were first performed at the Gamma point. Then the number of  $k$ -points was increased until the results were ascertained to be well converged. Altogether the positions of 30 atoms in the simulation cell were optimized in the total-energy minimization. The final, fully optimized structure (see Fig. 3) contained six relaxed layers and the Cl overlayer. Relaxation pulled the surface layers towards the bulk. The final optimized LDA structure predicts the Cl in the atop site with a Ge–Cl bond length

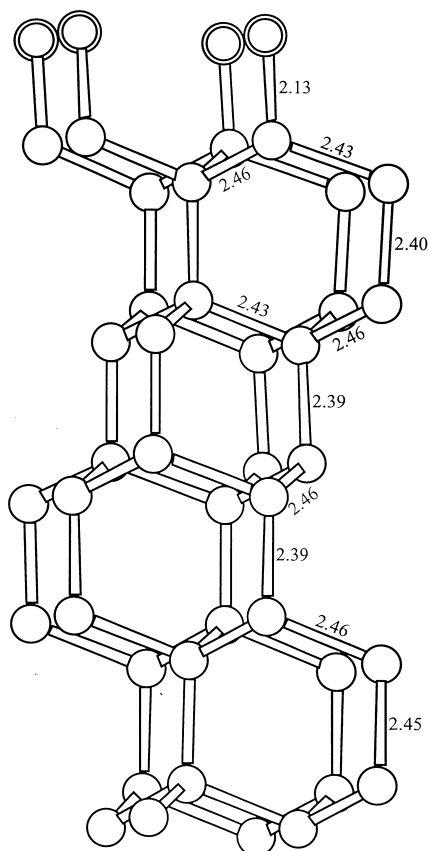


Fig. 3. Structure of the Cl-passivated Ge(111) surface derived from geometry optimization using first-principles LDA slab calculation. See text for details.

of  $2.131 \pm 0.005$  Å, where the uncertainty represents the statistical spread in the calculated bond lengths of the four chlorine atoms. The interplanar distances along the [111] direction were found to be contracted as compared with their bulk values. The calculated interplanar distances along [111] starting from the surface layer are 0.79, 2.41, 0.8, 2.41, 0.81, 2.42 Å, respectively, and then become the bulk values of 0.83 and 2.45 Å. An LDA calculation carried out by Bachelet et al. [15] in 1983 predicted a Ge–Cl bond length of  $2.07 \pm 0.03$  Å, in reasonable agreement with the present work. The difference in bond length of 0.06 Å may arise from different  $k$ -point sampling, different basis sets, pseudopotentials and different exchange-correlation potentials used.

The theoretical surface structure shown in Fig. 3 was used as the basis for a multiple scattering calculation of the Cl 1s EXAFS using Feff 6.01 [11]. 175 atoms were used to construct a six-layer cluster. The cluster was like that shown in Fig. 3, with a total extent normal to the surface of 15 Å. Contributions of multiple scattering paths up to 10 Å were included in the Feff 6.01 calculation. The XAFS signal was calculated for a range of Cl–Ge bond lengths between 2.10 and 2.20 Å and the results were compared with experimental values in order to find the optimum distance. The Cl–Ge bond is highly directional along the surface normal and there is a large difference between bond-stretching and bond-bending constants [16]. This implies a large difference in the Debye temperatures at these two directions. We used 350 K for the  $E_{\perp}$  polarization calculation. For the  $E_{\parallel}$  polarization, we found that 250 K provides the best fit to the amplitude of the experimental data. Fig. 4 compares the experimental XAFS data at both polarizations to the XAFS signal predicted by the Feff 6.01 calculation for the optimized structure (Cl–Ge distance of 2.16 Å). Excellent agreement between calculated and experimental XAFS was obtained. The high quality fit in both polarizations

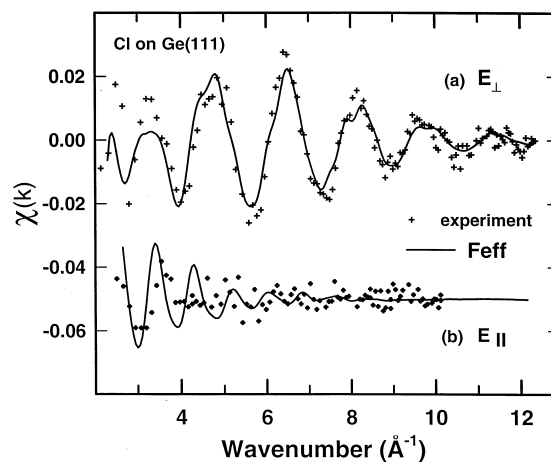


Fig. 4. Comparison (in wavenumber domain) of the unfiltered experimental XAFS (crosses) with that calculated using Feff 6.01 code (solid lines) at (a)  $E_{\perp}$  and (b)  $E_{\parallel}$  polarization. Note that an orientation-dependent Debye temperature was used (see text). The theoretical first-principles calculated surface structural model shown in Fig. 3 was used for the Feff calculation.

provides strong evidence that our calculated structural model is correct. The calculated curve fits the experimental data better at high wavenumbers ( $4\text{--}12\text{ \AA}^{-1}$ ) than at low wavenumbers ( $\leq 4\text{ \AA}^{-1}$ ). The relatively poor fit below  $4\text{ \AA}^{-1}$  is likely associated with the inaccuracy of Feff 6.01 multiple-scattering calculations at predicting near-edge (XANES) structure in open framework systems such as surfaces.

How does the measured Ge–Cl distance of  $2.17 \pm 0.01\text{ \AA}$  compare with that predicted by other methods? From our previous experience with LDA calculations for group IV as well as III–V materials [17–21] we expect the LDA approach to underestimate the bond length by about 1.5%. When this ‘correction’ is included, the predicted bond length becomes  $2.162\text{ \AA}$ , in excellent agreement with the present experimental result. A simple method to estimate the bond length is by adding covalent radii. The sum of the Pauling scale values for Ge ( $1.22\text{ \AA}$ ) and Cl ( $0.99\text{ \AA}$ ) [22] is  $2.21\text{ \AA}$ , in reasonable agreement.

### Acknowledgements

This work was supported financially by NSERC (Canada). We thank the staff of CSRF and SRC for enabling the synchrotron measurements and J. Lipkowski for generously loaning the X-ray detector. This work is based on research carried out at SRC, University of Wisconsin-Madison which is supported by NSF grant DMR 95-31009.

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