

**Polarization dependence of Ge(111)2×1 surface-state absorption  
using photothermal displacement spectroscopy:  
A test of surface reconstruction models**

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The polarization dependence of surface-state absorption of Ge(111)2×1 single-domain surfaces has been directly measured using photothermal displacement spectroscopy. The absorption at 0.5 eV is maximum for incident light polarized perpendicular to the period-doubling direction of the 2×1 reconstruction. As the polarization direction is rotated, the absorption follows a  $\cos^2\theta$  dependence. This result supports the  $\pi$ -bonded chain model for the surface reconstruction, and is the same as that recently reported for the dangling-bond absorption of Si(111)2×1.

The room-temperature cleavage surface of Ge(111) shows a metastable 2×1 reconstruction, with a low-energy electron-diffraction (LEED) pattern similar to that found on cleaved Si(111). Because of the chemical similarity of silicon and germanium, it has been generally assumed that the (111)2×1 reconstructions are the same for both materials. However, the stable, annealed structure for these surfaces is different, with germanium reconstructing to a 2×8 pattern and silicon to a 7×7 pattern. Recent angle-resolved photoemission (ARPES) results have opened a controversy regarding the similarity of the 2×1 reconstructions on cleaved silicon and germanium. Measurements by Nicholls, Hansson, Uhrberg, and Flodström<sup>1</sup> indicate a surface-state dispersion for Ge(111)2×1 which is similar to that reported for Si(111)2×1.<sup>2,3</sup> In particular, there is a strong (0.8 eV) dispersion along the  $\bar{\Gamma}$ - $\bar{J}$  direction of the surface Brillouin zone, rising at  $\bar{J}$  to near the bottom of the bulk energy gap. The ARPES measurements of Solal *et al.*,<sup>4</sup> on the other hand, show a band with relatively little dispersion along the  $\bar{\Gamma}$ - $\bar{J}$  direction which lies well below the valence-band maximum. This lower band is reminiscent of a second band seen in silicon.<sup>3</sup>

Several models for the reconstruction geometry of Si and Ge(111)2×1 surfaces have been proposed. The buckling model<sup>5</sup> proposes that alternate  $\langle\bar{1}10\rangle$  rows of atoms are raised and lowered, respectively, from their ideal bulk positions. The antiferromagnetic insulator model<sup>6</sup> finds the adjacent atoms to have alternating up and down spins. The  $\pi$ -bonded chain model<sup>7</sup> involves a rebonding of the top few surface layers to form  $\pi$ -bonded chains of atoms along the  $\langle\bar{1}10\rangle$  direction. A similar model proposed for diamond<sup>8</sup> involves a dimerized chain similar to the symmetric  $\pi$ -bonded chain but with alternate  $\pi$  bonds contracted and lengthened. The  $\pi$ -bonded molecule model<sup>9</sup> has a slightly different rebonding from the  $\pi$ -bonded chain, resulting in the  $\pi$ -bonded molecular axis close to the  $\langle 11\bar{2}\rangle$  direction. Total-energy calculations for both Si (Ref. 7) and Ge (Ref. 10) indicate the  $\pi$ -bonded chain model to be the minimum energy (111)2×1 structure of those tested. The band-structure calculations based on this model for Ge (Ref. 10) predict the dispersive band seen in the photoemission data of Nicholls *et al.*,<sup>1</sup> but do not agree with the results of Solal *et al.*<sup>4</sup>

Another important test of these reconstruction models is the predicted polarization dependence of the dangling-bond

optical absorption. This polarization dependence arises from symmetry considerations, and is not critically dependent on calculations requiring accurate atomic positions, such as those required to simulate photoemission or LEED data. The buckling and antiferromagnetic insulator models lead to a maximal absorption perpendicular to the rows of atoms with either position or spins up or down (along  $[11\bar{2}]$ ), with the absorption reduced by  $\frac{1}{3}$  along  $[\bar{1}10]$ .<sup>11</sup> The  $\pi$ -bonded chain model predicts strong absorption for light polarized parallel to the chains (along  $[\bar{1}10]$ ), and no absorption perpendicular to these chains, as they are well separated in space, leading to a  $\cos^2\theta$  dependence.<sup>12</sup> Dimerization of the chain rotates this  $\cos^2\theta$  dependence by the degree to which the major axes have been rotated by the dimerization.<sup>12</sup> The  $\pi$ -bonded molecule model leads to a maximal absorption along the molecular axis, or at a small angle to  $[11\bar{2}]$ .<sup>12</sup> Recent results on Si(111)2×1 with both photothermal displacement<sup>13</sup> and differential reflectivity<sup>14</sup> were shown to support the chain model.

We report here the first measurement of the polarization dependence of the Ge(111)2×1 surface-state absorption. We find the result to be the same as that found on silicon: a  $\cos^2\theta$  dependence, with a maximum along  $[\bar{1}10]$  as the incident polarization is rotated in a single-domain region reconstructed along the  $[11\bar{2}]$  direction. These Ge results were obtained with photothermal displacement spectroscopy,<sup>15</sup> which, unlike reflectivity measurements, directly measures the surface optical absorption without the need for a difference spectrum between clean and oxidized surfaces. We find a peak absorption of  $\sim 2\%$  at  $\sim 0.50$  eV. This agrees with the absorption previously observed via differential reflectivity using unpolarized light.<sup>16</sup> The spectrum is very similar to that found on Si(111)2×1, with a shift of  $\sim 40$  meV between the two surfaces.

Photothermal displacement spectroscopy is based on optical detection of the thermal expansion of a sample as it is heated by absorption of light. An optical absorption spectrum is generated as an intensity modulated, tunable light beam (pump beam) is focused onto the sample. Following the absorption of light, excited electrons decay nonradiatively and the sample is locally heated. The change in slope of the sample surface due to local thermal expansion is detected through the deflection of a HeNe probe beam, which is measured by a positron-sensitive photodiode. The signal, which is detected by phase-sensitive methods, is directly

proportional to the surface absorption coefficient of the sample and is easily calibrated.<sup>15</sup>

The experimental configuration is shown in Fig. 1. A Kr<sup>+</sup> pumped *F*-center laser serves as the pump beam. The laser beam is passed through a ZnSe  $\frac{1}{4}$ -wave Fresnel rhomb followed by a ZnSe Brewster-plate rotatable polarizer. The polarized beam is then focused by a CaF<sub>2</sub> lens through a CaF<sub>2</sub> ultrahigh vacuum (UHV) window onto the Ge crystal. The high-purity Ge crystal (impurities  $< 10^{11} \text{ cm}^{-3}$ ) was cleaved in UHV ( $\sim 3 \times 10^{-10}$  Torr) along the  $[1\bar{1}0]$  direction using the double-wedge technique. The pump and probe beams were aligned for a spatial resolution  $\sim 200 \mu\text{m}$  in the desired domain region as determined by LEED.

The surface optical absorption spectrum shown in Fig. 2 was measured with incident polarization along  $[1\bar{1}0]$ , or perpendicular to the period doubling  $[11\bar{2}]$  direction in a single-domain region determined by LEED. The polarization was rotated through  $360^\circ$  at a photon energy of 0.496 eV at the same point on the sample surface, with the results shown in Fig. 3. No absorption ( $< \frac{1}{30}$  of peak) was detected for light polarized parallel to  $[11\bar{2}]$ . There was no significant change in line shape or in the absolute magnitude of the photothermal signal when the polarizer was removed and the circularly polarized light was used to obtain a spectrum, indicating a uniform behavior of the polarization dependence over the energy region probed. After oxidation, the absorption was greatly reduced to less than  $\frac{1}{30}$  of the peak (see open circles in Fig. 3), confirming the surface as the source of this absorption.

We have also exploited the high spatial resolution of photothermal displacement spectroscopy to probe the variation of the polarization dependence of the surface-state optical absorption on cleaves which showed a varied domain structure. In a region with weak, multidomain LEED spots, an absorption which peaked at  $\sim 0.50$  eV was observed, but the polarization dependence was nearly isotropic, as would be expected for a symmetric superposition of domains. In a region which was predominantly reconstructed in the  $[12\bar{1}]$  direction, the polarization dependence was seen to rotate by  $120^\circ$  from the  $[11\bar{2}]$  region nearby. In regions which

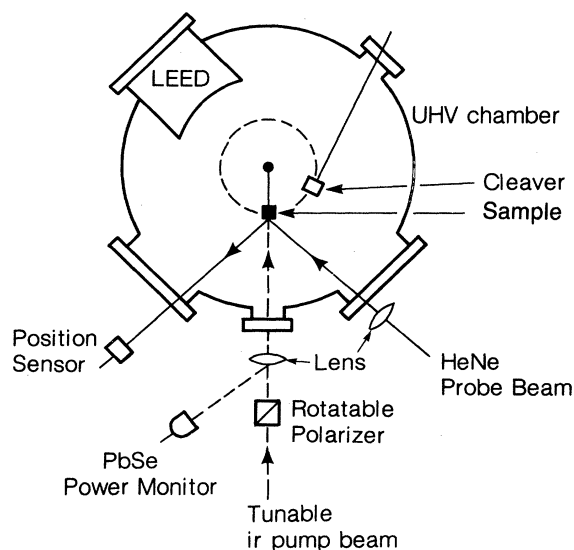


FIG. 1. Experimental configuration.

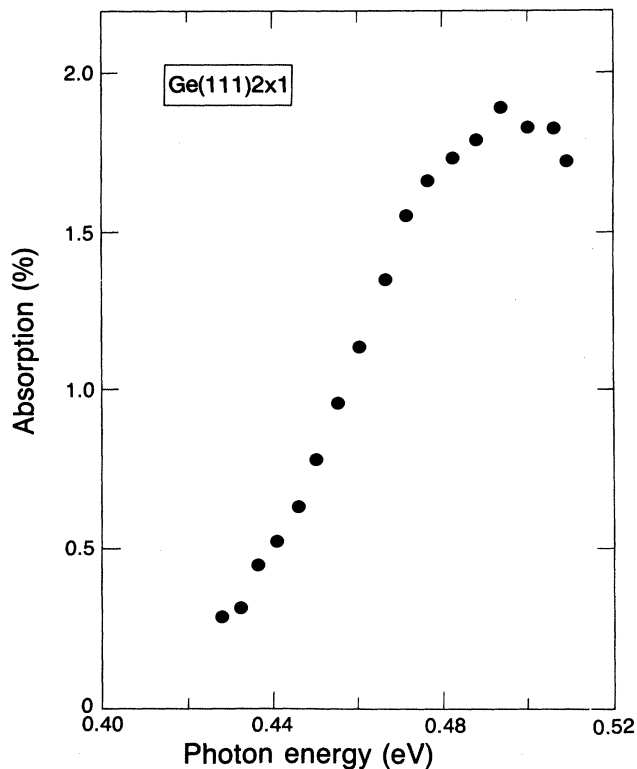


FIG. 2. Ge(111)2×1 surface-state-absorption spectrum. Incident light is polarized to  $[1\bar{1}0]$ .

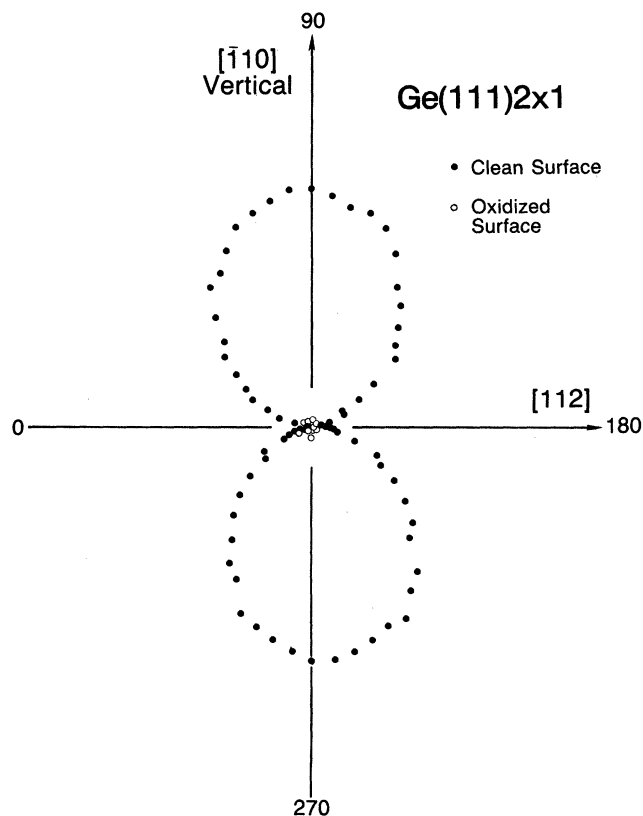


FIG. 3. Polar plot of the polarization dependence at 0.496 eV. Open circles were taken after exposure to  $10^4$  L ( $1 \text{ L} = 10^{-6}$  Torr sec) of O<sub>2</sub>.

showed second-order LEED spots from more than one domain, the polarization dependence could be fitted with a sum of  $\cos^2\theta$  rotated by  $\pm 120^\circ$ . To confirm the reliability of the system, the polarization dependence of absorption by a filter glass was measured and found to be isotropic with the same alignment that was used for the Ge results. These results indicate that the polarization dependence of Ge(111)2 $\times$ 1 surface-state absorption is correlated with the LEED structure in a consistent manner and is indicative of the surface symmetry.

The similarity of the results seen on Si(111)2 $\times$ 1 and Ge(111)2 $\times$ 1 surfaces with polarization-dependent photo-thermal displacement measurements indicates a similar reconstruction is occurring on the two surfaces. When the results are compared with the calculated polarization dependence for the various reconstruction models,<sup>11,12</sup> they indicate an agreement with the symmetric  $\pi$ -bonded chain model. A dimerization of the chains which results in less than  $\sim 5^\circ$  of rotation of the axes cannot be ruled out due to small uncertainties in the precise orientation of the sample relative to the polarizer.

The results presented here for the magnitude and position of the dangling-bond absorption are consistent with previous reflectivity<sup>16</sup> and electron-energy-loss experiments.<sup>17</sup> The polarization dependence of this absorption is consistent with the ARPES results of Nicholls *et al.*<sup>1</sup> which show a large dispersion along  $\bar{\Gamma}$ - $\bar{J}$  in the surface Brillouin zone, indicative of a strong overlap of dangling-bond orbitals along the  $[\bar{1}10]$  direction on the surface. Also, the presence of an occupied surface state near the bottom of the bulk (0.66 eV) energy gap is necessary for a surface gap  $\sim 0.50$  eV. The state measured by Nicholls *et al.*<sup>1</sup> was seen to be  $\sim 0.4$  eV below the Fermi level near  $\bar{J}$  on an *n*-type crystal, with a quoted energy resolution  $\leq 0.2$  eV. This state could serve as the ground state from which the surface optical absorption is generated, with an unoccupied surface state lying above the Fermi level. The surface state observed by Solal *et al.*<sup>4</sup> is less consistent with the data reported here. The

state is  $\geq 0.6$  eV below the Fermi level on a *p*-type sample, or  $\sim 0.5$  eV below the valence-band maximum, and could not serve as a ground state for the absorption measured here, as there are no unoccupied states within the surface gap energy. Although in principle the optical absorption could arise between the bulk valence band and an unoccupied surface state, this is unlikely due to peaked nature of the absorption.<sup>16</sup> It is possible that the energy of the surface state measured by Solal *et al.*<sup>4</sup> may be closer to the Fermi level in other regions of the surface Brillouin zone not reported in Ref. 4.

In conclusion, the polarization dependence of the dangling-bond optical absorption is an important test of reconstruction models. The results presented here using photo-thermal displacement spectroscopy are in agreement with only one model which has been proposed: the  $\pi$ -bonded chain model. If the  $\pi$ -bonded chain is found to be inconsistent with other experimental results, these polarization results indicate a highly anisotropic optical matrix element which must be incorporated into any future model for this surface. Finally, the similarity in the magnitude, dispersion, and polarization dependence of the optical absorption by Si(111)2 $\times$ 1 and Ge(111)2 $\times$ 1 support the premise that the two reconstructions are similar.

*Note added in proof.* Recent photoemission results of J. M. Nicholls *et al.* [Phys. Rev. Lett. 52, 1555 (1984)] confirm the earlier results of Ref. 1 and support the  $\pi$ -bonded chain model for Ge.

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