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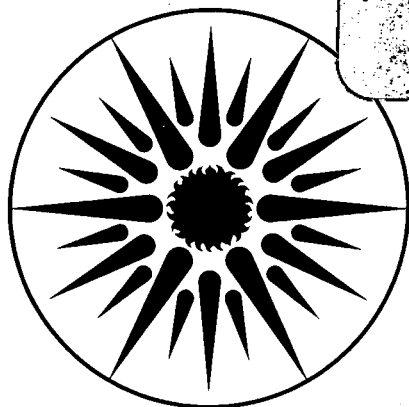
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*Invited Paper.*

**Polarization Dependent Ge and Si(111)2x1  
Surface State Optical Absorption:**

**A Test of Surface Reconstruction Models.**

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# POLARIZATION DEPENDENT Ge AND Si (111)2×1 SURFACE STATE OPTICAL ABSORPTION: A TEST OF SURFACE RECONSTRUCTION MODELS.

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## I. Introduction

The room temperature (111) cleavage faces of silicon and germanium are known to reconstruct to a metastable 2×1 unit cell, with period doubling along one of the three equivalent  $\langle 11\bar{2} \rangle$  directions on the surface. The mechanism behind this doubling of the unit cell has been the subject of much inquiry, with numerous models proposed to explain the various experimental results. Many of the results which have been used to distinguish among competing reconstruction models require extensive calculations for this process. Photoemission, ion backscattering, and LEED all require the assumption of a specific atomic configuration to generate theoretical results with which to compare the experimental data. The polarization dependence of the surface optical absorption, however, is a consequence of the overall symmetry of the dangling-bond orbitals, and does not require exact knowledge of the atomic positions to allow comparison with a class of models. As we will discuss below, the angular dependence of the dipole matrix element is different for the various models, making the polarization-dependent dangling-bond absorption a crucial test of these models.

We have studied the (111)2×1 surface state absorption of both Si and Ge using polarization-dependent photothermal displacement spectroscopy. In addition to investigating the room temperature cleaved surface, we have also monitored the temperature dependence of the surface absorption as it is changed during annealing of the Ge(111) surface from the 2×1 to the c-2×8 structure.

## II. Experimental Results

*A. Polarization Dependence.* The polarization-dependent dangling-bond absorption was measured using photothermal displacement spectroscopy.<sup>1,2</sup> In brief, photothermal displacement spectroscopy<sup>3</sup> involves the optical detection of the thermal expansion of a sample as it is heated by absorption of light. The change in slope of the surface due to local thermal expansion is detected through the deflection of a HeNe probe beam reflected from the sample. Among the advantages of this technique is the ability to measure surface absorption directly, without requiring a difference measurement between a clean and oxidized surface.

Both Si and Ge (111)2×1 surfaces exhibit a ~2% absorption of  $[\bar{1}10]$  polarized light, peaked at ~0.46 eV for Si and ~0.50 eV for Ge.<sup>1,2</sup> The polarization dependence of the absorption peaks for Si and Ge in single domain regions are shown in Fig. 1. A  $\cos^2\theta$  dependence with a maximum along  $[\bar{1}10]$  can be seen for both Si and Ge. The silicon results are in agreement with recent polarization dependent reflectivity measurements.<sup>4</sup> There is no significant rotation of the pattern, with all measurements being within experimental alignment error of  $\sim \pm 5^\circ$ . The pattern was observed to change when

areas of different or mixed domains were examined. It could always be fitted by

$\sum_{\beta_i=-1,0,1} a_i \cos^2(\theta + \beta_i \frac{2\pi}{3})$ , with the  $a_i$  correlating to the observed LEED intensities of the different domains. Of the various models discussed below, this is only consistent with the  $\pi$ -bonded chain model for both materials. The surface absorption disappeared upon oxidation as can be seen in Fig 1.

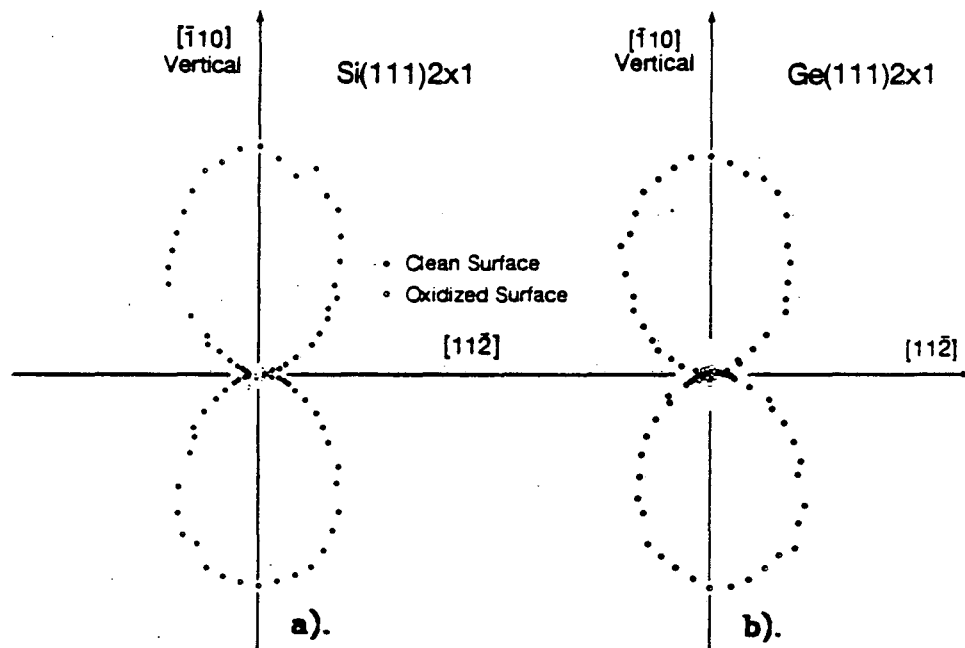


Fig. 1. Polarization dependence of (111)2x1 peak absorption for a.) Si (0.46eV) and b.) Ge (0.50eV).

**B. Temperature Dependence** The Ge(111) surface converts from 2x1 to a c-2x8 structure upon mild annealing, and preliminary results observing this phase transition via the polarization-dependent absorption as an order parameter are shown in Fig. 2. This particular cleave was not a single domain, but by fitting the polarization dependence it was determined that at the measurement point two domains were present in the ratio of ~12:1 with the primary absorption occurring for vertical polarization. The polarization of the incident light ( $\hbar\omega=0.48\text{eV}$ ) was alternated between vertical and horizontal during the annealing process, and the photothermal signal at the two polarizations is shown in Fig 2a. The spectrum and polarization dependence when half of the signal had been annealed away was indistinguishable from the original except in magnitude. The sample was then heated to 135°C, and as can be seen in Fig. 2, above ~105°C there was no significant polarization dependence. On the first cycle, the sample temperature was greater than 60°C, where the surface signal starts to diminish, for 40 minutes. On the second cycle, the time between the data points at 60°C and 105°C was 37 minutes.

Free carrier absorption can be seen contributing to the signal above room temperature. The surface signal can be extracted as the difference between the absorption of light polarized parallel and perpendicular to  $[\bar{1}10]$ , since the isotropic free carrier absorption adds equally to both polarizations (Fig. 2b). It is also possible to separate surface and bulk contributions through the phase of the photothermal signal.<sup>3</sup> The phase was observed to change smoothly from that of a surface absorption to the later arrival of the bulk signal between 60°C and 100°C. A vector separation of the two components was

found to be consistent with the polarization data shown in Fig. 2.

The 135°C anneal resulted in a diffuse, "weak  $8^{-5}$  LEED superstructure, and a subsequent 210°C anneal resulted in a sharp  $c-2 \times 8$  pattern. After the 210°C anneal, a small absorption at room temperature was detected at 0.48 eV. This absorption had a magnitude of  $\sim 0.06\%$  and no polarization dependence. Although the signal to noise ratio was low, the phase seemed to indicate surface origin. If so, it would indicate that the  $c-2 \times 8$  structure has a small absorption at this energy. This is consistent with surface photovoltage<sup>6</sup> (SPV) and photoconductivity<sup>5</sup> (SPC) measurements which find a signal at similar energies for the  $c-2 \times 8$  structure. The precise temperature dependence varies among cleaves, but the signal usually decays between 60°C and 130°C when the sample has been annealed just before cleavage. If the sample is not preannealed, the signal occasionally decays at 35°C-60°C, and the resulting LEED pattern is  $1 \times 1$ , probably due to contamination.<sup>5</sup>

### III. Discussion.

The polarization dependence of the dangling-bond absorption is proportional to the dipole matrix element between empty and full surface states as follows. The power absorbed from an incident light beam of photon energy  $\hbar\omega$  is given through the Fermi Golden Rule as

$$P_{\text{abs}} = \frac{\text{Absorbed Energy}}{\text{Time}} = \hbar\omega\Gamma = \hbar\omega \frac{2\pi}{\hbar} |H_{if}|^2 \delta(E_i - E_f - \hbar\omega)$$

with the transition matrix element involving the dot product of the photon vector poten-

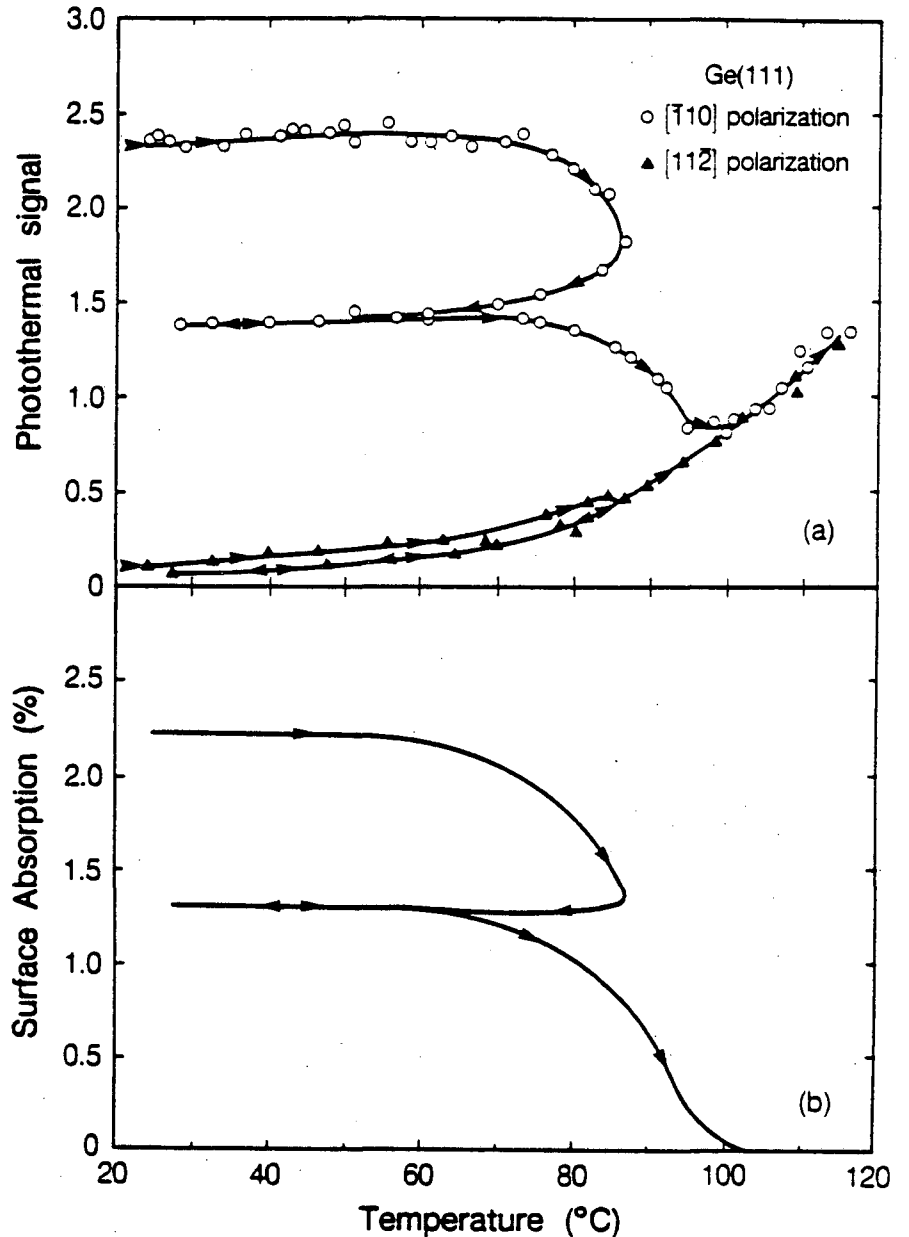


Fig. 2. a.) Temperature dependence of photothermal signal from cleaved Ge(111). Sample is heated, cooled and heated again. b.) Surface absorption. Difference between  $[\bar{1}10]$  and  $[11\bar{2}]$  signals in (a).

tial  $\mathbf{A}$  and the electron momentum operator  $\mathbf{p}$ :

$$H_{ef} = \langle \text{empty} | \frac{e}{mc} \mathbf{A} \cdot \mathbf{p} | \text{full} \rangle$$

thus:

$$P_{\text{abs}} = \frac{\pi e^2}{m^2 \omega} |E_{\text{loc}}|^2 |\hat{\mathbf{e}} \cdot \mathbf{p}_{ef}|^2 \delta(E_{ef} - \hbar\omega)$$

where  $E_{\text{loc}}$  is the local electric field at the surface with polarization vector  $\hat{\mathbf{e}}$ ,  $E_{ef}$  is the energy difference between empty and full surface states, and  $\hat{\mathbf{e}} \cdot \mathbf{p}_{ef}$  is the dipole (momentum) matrix element between the empty and full surface states. It is this matrix element that contains the useful information about the surface reconstruction, having different angular dependences for the various models discussed below.

The earliest model for the (111)2×1 reconstruction was proposed by Haneman<sup>7</sup> and involves a buckling of the surface, resulting in a charge transfer from the lowered to the raised atom. Until recently, the buckling model was invoked to explain the majority of existing experimental results. However, recent angle resolved photoemission (ARPES) results<sup>8,9</sup> were found to disagree strongly with the predictions of the buckling model. Also, a second band was occasionally seen<sup>9</sup> which was not predicted by the simple buckling model. This second band led to the inclusion of correlation effects in the theory of the buckling model,<sup>10</sup> which split each dangling-bond band into two bands of opposite spin, improving the fit to the ARPES data.

For these models, the dangling-bond optical absorption occurs between states localized on neighboring surface atoms. The vector connecting neighboring raised and lowered dangling bonds makes a 30° angle with  $[\bar{1}10]$  (denoted as  $\hat{\mathbf{x}}$ ), making the  $\mathbf{p}_x$  matrix element  $\approx \sqrt{3}\mathbf{p}_y$  (parallel to  $[11\bar{2}]$ ). This leads to a polarization dependence of the absorption with a ratio x:y of 3:1, and other angular effects lead to a somewhat dog-bone shaped polarization dependence.<sup>11</sup> This dependence does not change when correlation is or is not included, and is not strongly dependent on the size of the buckling. Also, any model involving limited movement of the surface atoms, such as a tilting of dangling bonds,<sup>12</sup> should have a similar polarization dependence, with light polarized parallel to  $\hat{\mathbf{x}}$  more strongly absorbed than that parallel to  $\hat{\mathbf{y}}$ . None of these models are consistent with the polarization-dependent absorption results, which show *no* absorption along  $\hat{\mathbf{x}}$ .

To explain the large dispersion measured in ARPES along  $\bar{\Gamma}-\bar{J}$  and the small dispersion in the orthogonal direction, Pandey<sup>13</sup> proposed that the top two surface layers rebond to form  $\pi$ -bonded chains along the  $[\bar{1}10]$  direction which are well separated in the  $[11\bar{2}]$  direction. The occasional appearance of the second band could be explained by an overlap of domain structures in the measuring area. Another explanation of this band was proposed by Chadi,<sup>14</sup> and involves a portion of the surface rebonding in the opposite direction, forming  $\pi$ -bonded dimers on the surface, perpendicular to the  $\pi$ -bonded chains.

For the  $\pi$ -bonded chain model, the one dimensional nature of the chain leads to a very strong polarization dependence of the absorption. For the mid-gap absorption between states along  $\bar{J}-\bar{K}$  in the surface Brillouin zone, there is no absorption at the peak



for light polarized perpendicular to the chains, with all of the absorption due to light polarized parallel to the chains.<sup>15</sup> This is the *same* polarization dependence as that measured experimentally. For the  $\pi$ -bonded molecule, the maximum absorption is for light polarized along the dimer bond, or at a slight angle to  $\hat{x}$ , with an approximately cosine squared pattern once again. This is not consistent with the data.

The  $\pi$ -bonded chain is thus the only one of these models which is consistent with the polarization dependence of the surface optical absorption. An additional experimental constraint on the  $\pi$ -bonded chain model is the size of the surface optical gap. In a symmetric chain, an optical gap between the bonding and anti-bonding orbitals along the chains arises only from the difference in third layer atoms beneath the surface atoms. An additional energy difference may originate from a buckling of the chain, as supported by total energy calculations of Northrup and Cohen<sup>16</sup> for both Si and Ge, or from dimerization, as proposed by Pandey for diamond.<sup>17</sup> A small buckling of the chain would not alter the polarization dependence in normal incidence; but in off-normal incidence, the vertical separation between the chain atoms leads to a non-zero  $p_z$  matrix element.<sup>15</sup> If the chain is dimerized, this rotates the symmetry axis and thus rotates the direction of the  $\cos^2\theta$  maximum from  $\hat{y}$ . This rotation is not seen experimentally, indicative of the absence of strong dimerization. The larger gap seen on Ge(111)2x1 than that of Si is consistent with total energy calculations finding a larger buckling along the chain on Ge than they do on Si.<sup>16</sup> Off-normal incidence absorption experiments are in progress to address the question of buckling along the chain more directly.

In addition to the polarization dependence of the dipole matrix element,<sup>1,4</sup> other data have also been found to be consistent with the  $\pi$ -bonded chain model for silicon, including ARPES,<sup>8,9</sup> angle resolved EELS,<sup>18</sup> and ion backscattering measurements.<sup>19</sup> A question still remains, however, in the explanation of the second ARPES band,<sup>9</sup> polarization-dependent surface photoconductivity<sup>20</sup> and LEED<sup>21</sup> data. For Ge, fewer experimental results are available, and there is disagreement between different groups on the ARPES data. Measurements by Nicholls *et al.* in 1983,<sup>22</sup> recently confirmed,<sup>23</sup> indicate a surface state dispersion for Ge(111)2x1 which is similar to that reported for Si(111)2x1, and consistent with the  $\pi$ -bonded chain model. The ARPES measurements of Solal *et al.*,<sup>24</sup> on the other hand, show a flatter band not predicted by the chain model.

The temperature dependence of the Ge(111)2x1 absorption is indicative of the phase transition on the (111) surface to the c-2x8 structure. This irreversible phase transition occurs slowly and over a wide temperature range, as has been noted previously during stepwise annealing.<sup>5</sup> The constant absorption lineshape during annealing can be interpreted to mean that the phase transition occurs in patches on the surface, leaving chains in the remaining regions which absorb in the same way as the clean surface.

In studying surface phase transitions, optical probes have the advantage of being non-intrusive and non-ionizing, avoiding risk of contamination or induction of the phase transition. However, unlike SPC and SPV measurements which must be made at low temperature, photothermal displacement spectroscopy yields data at elevated temperatures which can be directly related to the surface absorption. Also, even without the advantage of polarization to separate free carrier absorption from the surface absorption,

photothermal displacement spectroscopy is able to distinguish these components through the phase of the signal, unlike reflectivity, SPC and SPV.

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