

## Surface-Induced Optical Anisotropies of Single-Domain ( $2 \times 1$ ) Reconstructed (001) Si and Ge Surfaces

T. Yasuda, L. Mantese, U. Rossow, and D. E. Aspnes

*Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202*

(Received 1 August 1994)

We report surface-induced optical anisotropy spectra of clean ( $2 \times 1$ ) reconstructions of (001) Si and Ge surfaces, using oxygen exposure to separate contributions from dimers and steps. For Ge, the line shape is relatively simple and collapses uniformly with oxygen exposure. For Si, the results are more complicated and H termination must be considered as well. The clean-surface data of both Si and Ge are incompatible with a purely surface-to-surface transition model.

PACS numbers: 73.20.Dx, 78.66.Db

By capitalizing on crystal symmetry, above-band-gap surface- and interface-induced optical anisotropy (SIOA and IIOA) spectra are providing new insights into the physics and chemistry of buried interfaces, crystal surfaces during epitaxial growth, and boundaries in other non-ultrahigh-vacuum (UHV) environments where conventional surface-physics probes cannot be used [1–6]. While SIOA and IIOA sensitivities of less than 0.01 monolayer are now obtained routinely with reflectance-difference (-anisotropy) (RD and RA) spectrometers based on modulation-spectroscopic techniques, the calculation of accurate SIOA spectra remains a difficult theoretical challenge [7–15]. Optical anisotropies can arise in many ways, large numbers of atoms may be involved, and the results depend rather sensitively on local atomic structure, which is not known in sufficient detail under most conditions where reflectance-difference spectroscopy (RDS) has been applied. It is not even clear that the relevant mechanisms of these anisotropies have been identified.

Because RDS is becoming increasingly important in surface and interface analysis, it is essential that the appropriate theoretical capabilities be developed. To further this goal, we report SIOA spectra of the (001) surfaces of Si and Ge. The results are important not only because single-domain surfaces are preferred for heteroepitaxy, but also because the atomic structure of these reconstructions is well known [16–18]. Also, Si and Ge are elemental semiconductors, so ambiguities due to variations of surface stoichiometry cannot occur. Although SIOA data for (110) Si and Ge [1], H-terminated (001) Si [5], and the ( $2 \times 1$ ) reconstruction of (001) Ge [14] have been reported, the first two [1,5] were obtained under relatively poorly controlled surface conditions and the last [14] at low sensitivity with an uncertainty in sign. Thus the present results provide the first opportunity for a simple, yet critical, test of theoretical approaches.

Our experiments were performed on lightly doped ( $1-7 \Omega \text{ cm}$ )  $p$ -type Si and near-intrinsic  $n$ -type Ge wafers. The wafers were polished by the vendor and oriented  $4^\circ$  off (001) toward the [110] direction with accuracies of  $\pm 0.25^\circ$  and  $\pm 0.5^\circ$ , respectively. The Si wafers were cleaned by

a standard RCA procedure as described elsewhere [6]. The Ge wafers were degreased in trichloroethylene, acetone, and methanol, then lightly etched in a 1:2:5 solution of 1%  $\text{H}_2\text{O}_2$ : $\text{H}_2\text{O}$ :0.1% HF for 1 min at  $32^\circ\text{C}$ . After chemical cleaning, the samples were transferred via an oil-free pumped load lock into a UHV chamber with a base pressure in the low  $10^{-10}$  Torr range. The Si samples were then heated by a quartz-halogen lamp for 1 h at  $550^\circ\text{C}$  to rid the surface of C and for 2 min at  $920^\circ\text{C}$  to drive off O and form the ( $2 \times 1$ ) reconstruction. Background pressures during the  $920^\circ\text{C}$  anneal were in the low  $10^{-9}$  Torr range. For the Ge samples, C and O removal and the formation of the ( $2 \times 1$ ) reconstruction were accomplished by a single 2 min anneal at  $780^\circ\text{C}$ .

Surface cleanliness and the degree of suppression of ( $1 \times 2$ ) domains were assessed by Auger electron spectroscopy (AES) and reverse-view low-energy electron diffraction (LEED), respectively. Because the RDS contributions from ( $2 \times 1$ ) and ( $1 \times 2$ ) dimers cancel, for quantitative SIOA analysis it is essential that ( $1 \times 2$ ) domains be suppressed as much as possible and that this suppression be verified by an independent technique. Even though only those dimers in domains with characteristic dimensions larger than about  $100 \text{ \AA}$  will contribute to LEED [19], we can assume that if one type of domain is represented more strongly than this domain type exists preferentially on the surface. Scanning tunneling microscopy (STM) data suggest that ( $1 \times 2$ ) coverage is about 15% for a  $4^\circ$  vicinal surface [20]. Although these procedures are fairly standard for preparing ( $2 \times 1$ ) reconstructed surfaces, the results can be ambiguous because the monohydride surface also exhibits a ( $2 \times 1$ ) LEED pattern and AES is not sensitive to H.

Oxygen exposures were performed under turbomolecular pumping with sample temperatures of the order of  $70^\circ\text{C}$ . The ion pumps were valved off during this procedure to avoid contaminating the surface with by-products that are generated when these pumps are exposed to high fluxes of  $\text{O}_2$ . RD data were obtained as described previously [21] and recorded as  $\Delta\tilde{r}/\tilde{r} = \Delta r/r + i\Delta\theta = 2(\tilde{r}_\alpha - \tilde{r}_\beta)/(\tilde{r}_\alpha + \tilde{r}_\beta)$ , where  $\tilde{r}_\alpha$  and  $\tilde{r}_\beta$  are the complex

near-normal-incidence reflectances for light polarized parallel to the principal axes  $\alpha$  and  $\beta$ , respectively, in the plane of the surface. For the  $(2 \times 1)$  reconstruction the dimers are parallel to the  $[\bar{1}10]$  step edges and we take  $\alpha$  and  $\beta$  to be the  $[\bar{1}10]$  and  $[110]$  directions, respectively. Because all signals are relatively small, we took particular care to eliminate the effects of residual strain in the UHV-compatible window, especially for  $\Delta\theta$ , which is affected more strongly than  $\Delta r/r$ .

Representative LEED data for the (001) Si surface prepared as described above and taken at 56 eV are shown in Fig. 1. The  $(2 \times 1)$  pattern is strong, and the spots are split as expected along the step direction. However,  $(1 \times 2)$  half-order spots are still apparent. Although a quantitative measure of the relative coverages of  $(2 \times 1)$  and  $(1 \times 2)$  dimers from these data would be desirable, this information cannot be resolved given the present experimental configuration because the response of the photographic film is nonlinear and dimers in small domains do not contribute to the LEED spot intensity as discussed above.

Representative SIOA spectra  $\Delta r/r$  for the  $(2 \times 1)$  reconstructions of (001) Ge and Si are shown in Figs. 2 and 3, respectively. The amplitudes of these SIOA data are about the same as those of (001) surfaces of III-V semiconductors [2-5] but about a factor of 5 smaller than those of the (110) surfaces of Si and Ge [1,6]. For reference, we also show the nearly null spectra that were obtained before the surfaces were processed thermally. In this case the anisotropy is extremely small due to a near cancellation of nearly equal surface contributions from the two spatially inequivalent, but chemically identical, sublattices of the diamond structure. This residual anisotropy illustrates the sensitivity of our spectrometer and the degree to which experimental artifacts such as window-strain effects have been eliminated.

We first consider the results for Ge. For the  $(2 \times 1)$  reconstruction the largest amplitudes are obtained for surfaces with the least amount of C as determined by AES. C simply reduces the amplitude without changing

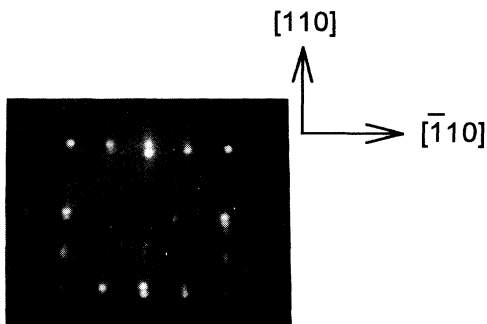


FIG. 1. LEED data for the (001) Si surface prepared thermally as described in the text. The beam energy was 56 eV. The data for (001) Ge are similar.

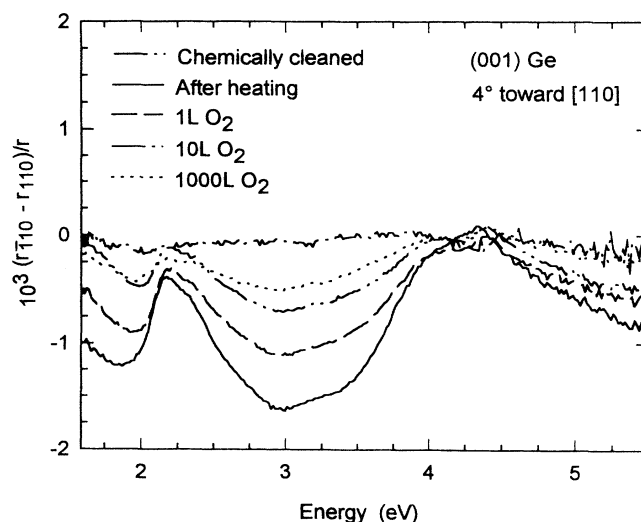


FIG. 2.  $\Delta r/r$  spectra for (001) Ge. Solid line: thermally prepared surface. Remaining lines: oxygen exposures as indicated. The nearly null spectrum is that of the chemically prepared surface.

the line shape. The data shown in Fig. 2 are about  $\frac{2}{3}$  the maximum that we have observed, indicating the presence of some residual C. When the sample is exposed to oxygen, the entire spectrum collapses uniformly along with the intensity of the half-order LEED spots. At 1000 L these spots vanish completely, leaving only a  $(1 \times 1)$  pattern. This indicates that the oxygen attacks the terrace dimers. The corresponding uniform collapse of the SIOA signal shows that this signal originates with the dimers and that the steps contribute little or nothing. Although a residual SIOA response remains even after the LEED pattern has vanished, this can be expected because long-range order will be destroyed well before all dimers have been eliminated.

SIOA spectra for the  $(2 \times 1)$  reconstruction of (001) Ge surfaces have been reported by Wormeester *et al.* [14]. Their spectra were deduced by comparing ellipsometric data of clean and oxidized  $5^\circ$  vicinal surfaces. Since oxidized vicinal (001) surfaces are essentially optically isotropic, their data are related to ours as  $\delta(\tan\psi) = \Delta r/r$ . Our data were obtained with substantially less noise and better resolution, as evidenced by our observation of structure at the bulk  $E_1$  and  $E_1 + \Delta_1$  energies of 2.1 and 2.3 eV, respectively, but otherwise the overall line shapes agree. Their amplitudes are 20% greater than our largest, which we attribute to a more nearly single-domain surface that resulted from their greater vicinal angle. However, the sign of their  $\delta(\tan\psi)$  data is ambiguous, which led to an incorrect choice of sign for the surface dielectric anisotropy derived from these data.

The sign correction has significant implications for SIOA mechanisms, as follows. As described and/or

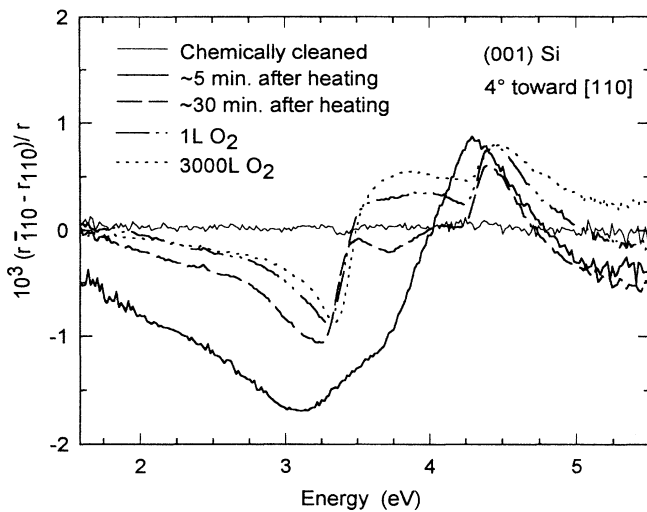


FIG. 3. As Fig. 2, but for Si.

derived in Ref. [14], the energies of the  $(2 \times 1)$  Ge surface states are known from photoemission and STM results, and their symmetries from a combination of theory and experiment. This information is linked to  $\Delta r/r$  by

$$\begin{aligned} \Delta r/r &= \text{Re}\{(\bar{r}_{\bar{1}10} - \bar{r}_{110})/\bar{r}\} \\ &= (4\pi/\lambda) \text{Im}[(\epsilon_{\bar{1}10} - \epsilon_{110})d/(\epsilon_s - 1)], \quad (1) \end{aligned}$$

where  $(\epsilon_{\bar{1}10} - \epsilon_{110})d$  is the SIOA,  $\epsilon_s$  the substrate dielectric function, and  $\lambda$  the wavelength of light. Below about 2.1 eV the only allowed surface-to-surface transitions are those for light polarized along the  $[\bar{1}10]$  direction [14]. Since  $\text{Im}(\epsilon)$  is positive definite and in this energy range  $\epsilon_s$  is essentially real, then according to this model  $\Delta r/r$  should be positive, contrary to the data of Fig. 2. Consequently, a purely surface-to-surface transition model is not tenable. Viable SIOA models must include surface-to-bulk, bulk-to-surface, and bulk-to-bulk transitions, as well as surface-to-surface transitions as previously discussed by Manghi *et al.* [9]. A more complicated origin is also implied by the 2.1, 2.3 eV bulk fine structure mentioned above.

We next consider the SIOA data of Si, shown in Fig. 3. The solid-line spectrum is that which is obtained immediately after thermal processing. It evolves with time into the dashed line shape. Heating reverses the process, aside from a decrease in amplitude due to carbon accumulation. In both cases a  $(2 \times 1)$  LEED pattern is observed. While it would appear that the initial spectrum represents that of the clean surface, there are several possibilities for the second including (a) adsorption of atomic hydrogen [22] generated, for example, by the ion pumps and (b) a phase transition to the  $p(2 \times 2)$  or  $c(4 \times 2)$  state [23,24]. To provide further information we exposed the surface to oxygen with the sample at room

temperature. After 1 L the higher energy features broaden and collapse, but the 3.4 eV feature sharpens and shifts to higher energy. Further exposure up to 3000 L has little additional effect. Even at 3000 L the half-order  $(2 \times 1)$  LEED spots remain, showing that the surface is still dimerized. This resistance of dimers to oxidation suggests that the limiting spectrum pertains to the monohydride phase [25], with the rapid change upon initial oxidation being due to steps.

To examine the step signal more clearly, we subtract the dashed curve from the 1 L spectrum. The result, shown in Fig. 4, exhibits negative peaks near 3.4 and 4.4 eV. This difference is similar to that observed when an initially oxidized  $(113)$  surface is thermally annealed, which has been interpreted as an effect arising from step disorder [6]. Further, we suppose that these data originate from a step-induced dichroism of the bulk transitions that is localized at the surface. When substituted into the *surface* expression, Eq. (1), the assumption of 40 meV  $\text{\AA}$  for the threshold-thickness product  $(E_{g,\bar{1}10} - E_{g,110})d$ , where the transition associated with  $[\bar{1}10]$  polarization moves relatively to higher energy upon oxidation, yields excellent agreement especially near the 3.4 eV transition, thereby supporting the interpretation. The clean spectrum does not show this sharp 3.4 eV peak, which suggests that the step reconstruction is particularly sensitive to adsorbates.

In comparing the spectra of Ge and Si dimers we find substantial line shape agreement near the  $E_2$  peak. However, the line shapes behave differently near the  $E_1$  and  $E_1 + \Delta_1$  transitions, since a sharp peak occurs near 2.2 eV for Ge and only a broad feature at 3.4 eV for Si. Since Si is essentially transparent below 3.4 eV, the observation of a negative  $\Delta r/r$  here indicates the presence of substantial surface optical absorption along the  $[\bar{1}10]$

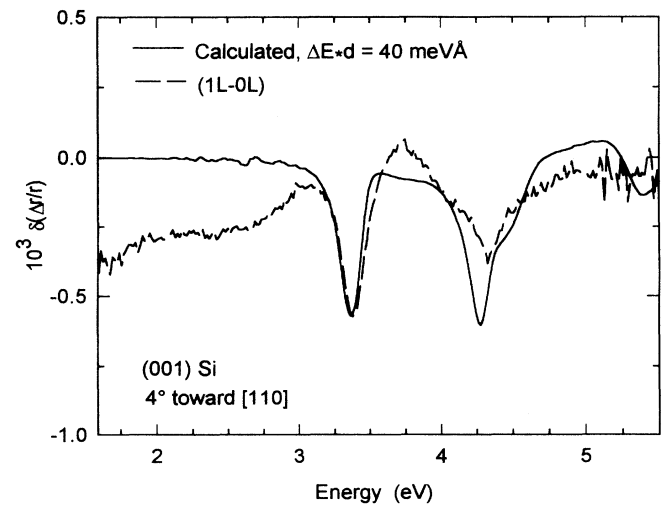


FIG. 4. Solid line: difference between 1 and 0 L spectra of Fig. 3. Dashed line: spectrum calculated by assuming a dichroism that is limited to the surface.

direction. We have also investigated the applicability of the surface-transition model for the  $(2 \times 1)$  reconstruction of (001) Si and have found that, as with (001) Ge, the data are inconsistent with surface-to-surface transitions alone. In contrast to the (110) surfaces, these (001) spectra do not appear to have any simple interpretation, even on a phenomenological level [7].

SIOA spectra for the  $(2 \times 1)$  reconstruction of (001) Si have been calculated by Wijers *et al.* [11,12] and by Shkrebtii and Del Sole [13]. Both groups obtained similar results, and their calculated spectra agree qualitatively with those reported here. However, quantitative agreement is still lacking. The difficulty of calculating SIOA spectra from first principles can be appreciated from existing results, which include not only those of Refs. [11–13], but also those of Mochàn and Barrera [8] for adsorbates on (110) Si and Ge and Chang and co-workers [10] and Morris *et al.* [15] for (001) GaAs. All show a very high sensitivity to atomic position, especially with respect to bond distortions and local-field effects. For example, Shkrebtii and Del Sole [13] show that the main low-energy structure for asymmetric dimers is 0.7 eV lower in energy than that for symmetric dimers. Consequently, SIOA line shapes should be an excellent probe of structural details once theoretical calculations become sufficiently accurate to predict them. The present work is intended to stimulate progress in this direction.

It is a pleasure to acknowledge support of this work by the Office of Naval Research under Contract No. N00014-93-1-0255, and of further support of U. R. by the Alexander von Humbolt Foundation. We also appreciate L. Kipp and D. Biegelsen for pointing out the possibility that our original (001) Si data could have corresponded to the monohydride phase.

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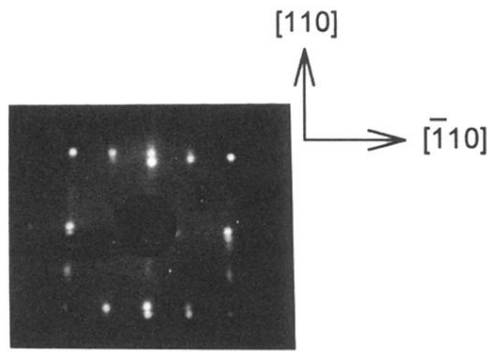


FIG. 1. LEED data for the (001) Si surface prepared thermally as described in the text. The beam energy was 56 eV. The data for (001) Ge are similar.