Anisotropies in the Above–Band-Gap Optical Spectra of Cubic Semiconductors

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(Received 24 August 1984; revised manuscript received 1 March 1985)

We report the first systematic study of above–band-gap optical anisotropies in cubic semiconductors. The anisotropies are large, of the order of 1%. The dominant intrinsic contributions for (110) Si and Ge are due to surface many-body screening and bulk spatial dispersion. Extrinsic contributions from chemisorbed and physisorbed species also play important roles.

PACS numbers: 78.20.Dj, 73.20.Cw, 78.40.Fy, 81.40.Tv

Optical anisotropies of electronic origin have been important for isolating surface- from bulk-related optical processes in the below–band-gap absorptance[1] and reflectance[2] spectra of semiconductors and in the reflectance[3] and ellipsometric[4] spectra of metals. The approach takes advantage of crystal symmetry by suppressing by subtraction the dominant, but unwanted, nominally isotropic optical contribution from the bulk. As in second-harmonic generation,[5] a relative enhancement of processes occurring at the lower-symmetry surface region results. While bulk properties of cubic materials are not strictly isotropic, refractive index anisotropies for (110) Si[6] and GaAs[7] show that relative below–band-gap bulk reflectance anisotropies should be $\sim 4\times 10^{-6}$ compared to $\sim 4\times 10^{-2}$ for the band-gap surface state on the 2×1 (111) surface of Si.[2] This suggests that optical anisotropies should also be useful for studying above–band-gap surface properties of semiconductors.

Surprisingly, except for a single exploratory spectrum reported nearly twenty years ago for (110) Si,[8] no such data are available. We report the first systematic investigation of these anisotropies. We find that they arise from at least five separate mechanisms. The dominant intrinsic contributions are due to surface many-body screening and bulk spatial dispersion. Extrinsic contributions from physisorbed molecules, chemisorbed species, and microstructured overlayers have also been identified.

The data reported here were obtained by reflection of linearly polarized light at near-normal incidence (10° off normal, p polarization) from specular surfaces of rotating samples and phase-sensitive detection of the second harmonic of the mechanical rotation frequency in the reflected beam. Surfaces were prepared as described previously,[9] and were maintained in a dry N_2 atmosphere to minimize contamination. The detector output was monitored to ensure that no macroscopic defects affected the sinusoidal component. Results are expressed as relative reflectance-difference (RD) spectra $(R_\alpha - R_\beta)/R$, where the subscripts α and β refer to the principal orthogonal axes of the anisotropic bulk and/or surface phases, and R is the average value $(R_\alpha + R_\beta)/2$.

Figure 1 shows RD spectra for a naturally oxidized (110) Si wafer with a carrier concentration $n = 2\times 10^{14}$ cm^{-3}, and for the same wafer with the oxide removed by buffered HF (BHF). The principal axes were established by anisotropic etching.[10] The reflectance difference is small below the E_1 direct-transition threshold near 3.4 eV but reaches a maximum of nearly 1.5% at the 4.3-eV E_2 peak in ϵ_2. The effects are reversible, with the original spectrum being recovered if the stripped surface is reoxidized naturally in air.

The oxidation change is shown explicitly at the bottom of Fig. 1 together with that observed when the stripped surface is exposed to a 3 vol% solution of Br_2 in methanol. By the usual surface-physics arguments, these changes are due to surface effects. The similarity of the changes induced by Br_2 and O_2 implies either that the surface electronic polarizability is unaffected by the specific oxidant used to terminate the (110) Si

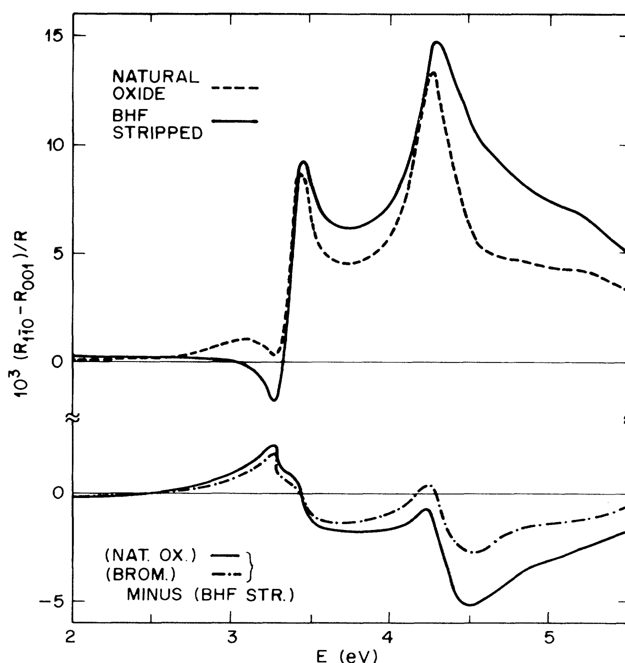

FIG. 1. Top: RD spectra for a naturally oxidized (110) Si surface before and after stripping with buffered HF (BHF). Bottom: changes in the stripped-surface spectrum upon air oxidation and upon exposure to Br_2 in methanol.

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surface, or that O_2 oxidation is promoted by Br_2. Changes in space-charge electric fields can be eliminated as a major cause since electroreflectance spectra for Si are much smaller and sharper.[11] Since theoretical descriptions of the electronic properties of chemically treated surfaces are lacking, we limit our discussion of chemically induced changes to qualitative remarks.

Figure 2 shows RD data for a (110) Ge wafer with $n = 3\times 10^{16}$ cm^{-3}. The line shape is similar to that for (110) Si, but now virtually no change occurs if the H_2O-stripped surface is oxidized naturally in air. Thus while H_2O readily dissolves GeO_2, it evidently fails to remove oxygen bonded to the outermost plane of Ge atoms. Also, Br_2 causes no changes except in the 2.0- to 3.5-eV spectral range.

The phenomenological description of these data is simplified because the observed ansiotropies, while large enough for easy measurement, are small enough to treat to first order in the optical functions. Reflectance differences of bulk origin can be described to first order in $\epsilon_{\alpha\alpha} - \epsilon_{\beta\beta}$ by the modulation-spectroscopy equation:

$$\frac{R_\alpha - R_\beta}{R} = \mathrm{Re}\left[\frac{2n_a(\epsilon_{\alpha\alpha} - \epsilon_{\beta\beta})}{n_s(\epsilon_s - \epsilon_a)}\right], \quad (1)$$

where $\epsilon_{\alpha\alpha}$ and $\epsilon_{\beta\beta}$ are the components of the dielectric tensor along α and β, and $\epsilon_s = n_s^2$ and $\epsilon_a = n_a^2$ are the average dielectric functions and refractive indices of the bulk and ambient phases, respectively. Reflectance differences of surface or thin-film origin can be described to first order in d/λ by the three-phase model:

$$\frac{R_\alpha - R_\beta}{R} = \frac{8\pi d}{\lambda}\,\mathrm{Im}\left[\frac{\epsilon_{\alpha\alpha} - \epsilon_{\beta\beta}}{\epsilon_s - \epsilon_a}\right], \quad (2)$$

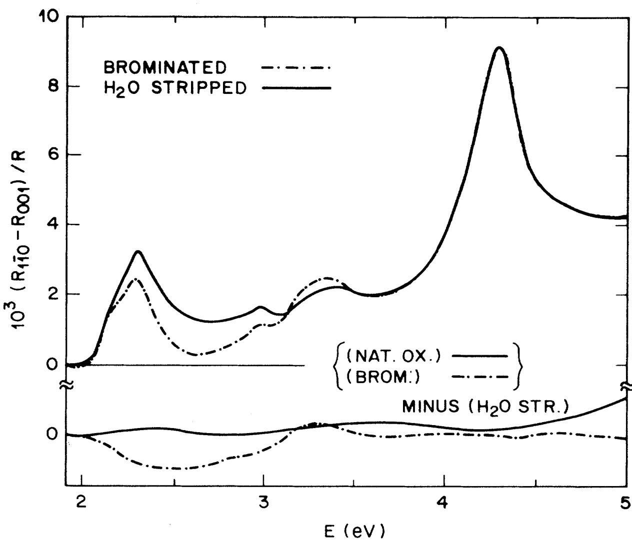

FIG. 2. As Fig. 1, but for (110) Ge.

where $\epsilon_{\alpha\alpha}$ and $\epsilon_{\beta\beta}$ now refer to the surface or thin-film phase, d is the effective thickness of the phase, and λ is the wavelength of light.

We now examine the results from Br_2-treated H_2O-stripped (110) Ge in more detail. The changes occur in the spectral range corresponding to optical extinction in gas-phase Br_2,[12] implying that bromine is physisorbed on this surface in molecular form. We now perform a Kramers-Kronig analysis and use Eq. (2) to calculate $(\epsilon_{1\bar{1}0} - \epsilon_{001})d$ directly. We next calculate the equivalent spectrum from gas-phase extinction data for Br_2 assuming an areal density of 1 Br_2 molecule per surface Ge (approximately the density of solid Br_2). The results are shown in Fig. 3. Structure from the dominant $B\,^3\Pi(0_u^+) \leftarrow X\,^1\Sigma_g^+$ and $^1\Pi(1_u) \leftarrow X\,^1\Sigma_g^+$ transitions at 2.5 and 3.0 eV, respectively, of the Br_2 molecule are seen in both spectra. If the Br_2 spectrum is doubled in amplitude and phase shifted by 45°, the agreement with the measured RD change spectrum is very good. Thus the identity of the physisorbed layer as Br_2 appears established.

The observation of a molecular Br_2 response is independent *chemical* evidence for the existence of a residual oxide layer, since Br_2 does not attack semiconductor oxides. The observation of the response in a reflectance *difference* spectrum shows that the Br_2 is physisorbed in a preferred orientation. Since Br_2 absorption vanishes for light polarized perpendicular to

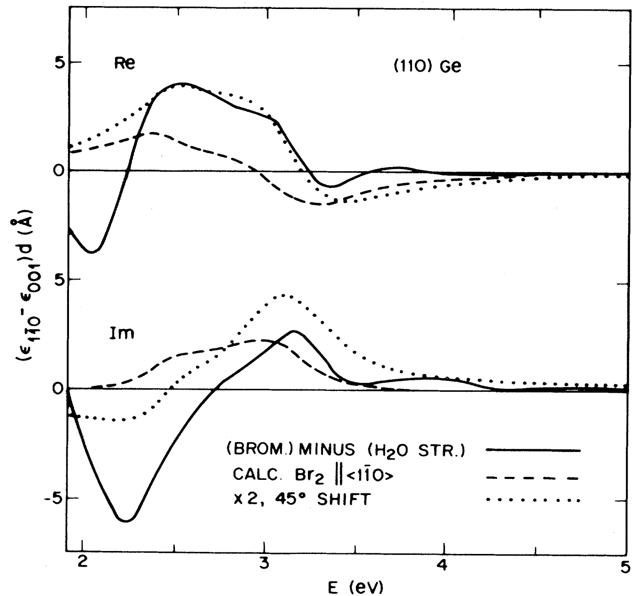

FIG. 3. Solid lines: Surface anisotropy calculated from the dash-dotted spectrum at the bottom of Fig 2. Dashed lines: equivalent spectrum calculated from gas-phase extinction data of Ref. 12. Dotted lines: same spectrum shown two times larger and phase-shifted by 45° to illustrate optical structure more clearly.

the molecular axis, the preferred orientation is that with the molecular axes parallel to $\langle 1\bar{1}0\rangle$. Thus the residual oxide cannot be thick enough to lose bulk registry, i.e., the outer Ge atoms are probably terminated by bonds to single oxygen atoms with little or no oxygen penetration below the outer Ge plane. These results also imply that BHF effectively removes most or all surface oxygen from (110) Si.

We consider next the mechanisms giving rise to the "intrinsic" or background RD line shapes for the (110) Si and Ge surfaces. The oxidized-surface spectra bear a striking resemblance to the imaginary parts of ϵ_s for the respective materials,[13] except that the critical-point structures are exaggerated. This indicates at least two contributions, the first of the form $\mathrm{Im}(\epsilon_s)$ and the second of a first-derivative nature. The imaginary projection suggests a surface phenomenon, which by Eq. (2) must scale as ϵ_s^2. To obtain this dependence, we take the resolvent of the Dyson equation to express ϵ_s in terms of the one-electron dielectric response, $\epsilon_{\mathrm{s.o.}}$, and a screening parameter, g, representing many-body corrections[14]:

$$\epsilon_s = \epsilon_{\mathrm{s.o.}} - \epsilon_s g \epsilon_{\mathrm{s.o.}}. \tag{3}$$

The importance of these many-body corrections in the optical spectra of semiconductors is well documented.[15] If we now assume that the screening is slightly different in the vicinity of the surface, then $g \to g + \Delta g$ and a small-term expansion of Eq. (3) yields $\Delta\epsilon_s = -\epsilon_s^2 \Delta g$. If this change is anisotropic, the desired result is obtained. Thus the intrinsic (110) Si and Ge RD line shapes are a direct manifestation of surface many-body screening.

Two explicit models can be cited. In a recent local-field calculation,[16] Mochan and Barrera predicted large optical anisotropies arising from the truncation of lattice sums over induced dipoles because of the presence of a surface. These anisotropies can be evaluated explicitly[16] for an fcc lattice to give $R_{1\bar{1}0} - R_{001} \cong 0.9 \times (a_0 E/hc)\,\mathrm{Im}(\epsilon_s)$. The rapid convergence of dipole sums shows that the effect is a true surface phenomenon, being localized to the outermost two or three atomic planes. A similar expression can be derived from the contact-exciton formalism[14] except that the line shape is proportional to E^3 instead of E.

We consider next the first-derivative contribution. Bulk spatial dispersion effects can be calculated by displacement of the valence and conduction bands relative to each other by an amount proportional to q^2, where q is the wave vector of the photon.[17] The result is a first-derivative spectrum with the resulting line shape proportional to $q^2 = \epsilon_s E^2$. The scaling factor can be evaluated for the E_1 structures with standard selection rules, and for Si we find from Eq. (1) that $\Delta R/R = [E^2/(10^6\ \mathrm{eV})]\,\mathrm{Re}(n_s^{-1} d\epsilon_s/dE)$.

Using these line shapes, we obtain a good representation of the RD spectrum for the oxidized (110) Si surface, as shown in Fig. 4. A similar good fit is obtained for (110) Ge. Separate scaling factors were used in the E_1 and E_2 spectral regions since the theoretical scaling factors depend on selection rules and wave-function normalizations that change over the Brillouin zone. The surface local-field line shape gives a better representation near E_1 and the surface contact exciton line shape near E_2 for both Si and Ge, although the differences are not significant. This near equivalence is not surprising, since both models describe surface many-body screening. The overall agreement indicates that the major intrinsic contributions have been identified.

The individual contributions shown at the bottom of Fig. 4 indicate that about $\frac{2}{3}$ of the intrinsic contribution comes from surface screening and $\frac{1}{3}$ from bulk spatial dispersion. Using the amplitudes determined from the fitting procedure and the magnitudes of the surface local field and bulk energy-band effects estimated above, we find that the surface local-field and bulk spatial-dispersion models overestimate and underestimate, respectively, the observed amplitudes in the vicinity of the E_1 transitions by about an order of magnitude. The discrepancies are in the expected direction; the former because local-field effects are considerably overestimated by the assumption of point-polarizable species, and the latter because the one-electron approximation consistently underestimates oscillator strengths.

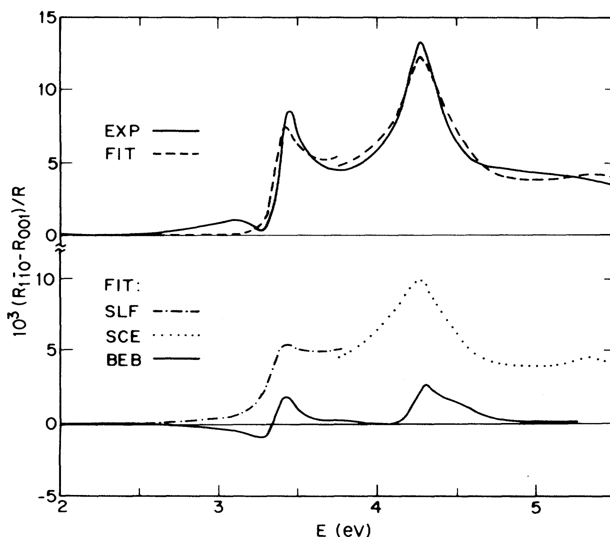

FIG. 4. Top: comparison between experimental and best-fit RD line shapes for oxidized (110) Si. Bottom: contributions from surface screening and bulk spatial dispersion. SLF, SCE, and BEB refer to surface local-field, surface contact-exciton, and bulk energy-band models, respectively.

With the intrinsic line shape identified, we can now conclude that the *oxidized,* not stripped, (110) Si surface is the one for which surface-state contributions are minimized in this spectral range. Consequently, the RD-change spectrum at the bottom of Fig. 1 is the line shape characteristic of surface polarizability. A similar good fit to the RD data for the H_2O-stripped (110) Ge surface, which we have also shown possesses a residual oxide overlayer, is consistent with this interpretation.

In conclusion, we have demonstrated that optical anisotropies in above–band-gap near-normal-incidence reflectance spectra of cubic semiconductors offer new possibilities in surface and interface analysis. Surface many-body screening should be even more important in direct reflectance and ellipsometric spectra, and should lead to interesting and unusual effects in the optical properties of adsorbates on, and interfaces with, semiconductor surfaces. These previously unsuspected anisotropies are larger than presently attainable accuracies in spectrophotometry and spectroellipsometry; hence further reports of measured optical properties in cubic materials must also specify azimuthal orientation of the plane of incidence as well as crystal face. Finally, a complete analysis of these effects awaits the development of a satisfactory theory of the relatively large surface chemical contributions. The present data should stimulate work in this direction.

We are grateful to M. Cardona and W. L. Mochan for useful correspondence.

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