

NONLINEAR ELECTROREFLECTANCE IN SILICON AND SILVER*

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The intensity of second harmonic light produced in reflection by a laser beam incident on silver and silicon surfaces shows a significant variation when a dc electric field is applied normal to the surface. Experimental data on the intensity, polarization, and dispersive properties of the induced surface harmonic polarization are presented and discussed.

Second-harmonic reflected light from silver¹ and silicon² surfaces has been observed. It is caused predominantly by a quadrupolar-type nonlinearity from both bound and free electrons, involving intra- and interband transitions.³ It is well known that the second-harmonic production in crystals with inversion symmetry, such as calcite, can be enhanced by the application of a dc electric field.^{4,5} It is also known that the linear optical-reflection coefficient of semiconductors can be changed by the application of a dc electric field. This electroreflectance effect^{6,7} is caused by a variation of the joint density of states in the neighborhood of the critical points, when an external parameter such as the applied electric field is modulated. Differential variations of the linear reflected intensity of about 1 part in 10^4 have been observed for several semiconductors^{8,9} and for silver.¹⁰ A convenient technique to apply the large dc field⁷ is to immerse the sample in an electrolyte solution with a small bias voltage between it and a platinum electrode.

Combination of these facts suggests that the intensity of the harmonic reflected light may be changed by the same technique. Experimental observation of this effect was briefly mentioned earlier.³ In this note we report on the striking variations in the second-harmonic intensity and its polarization characteristics as a function of the dc bias voltage. A pulsed ruby-laser beam at 6940 \AA entered a cell containing a $0.1N$ KCl solution and hit the immersed sample surface at an incident angle of 45° . The reflected second-harmonic intensity was observed in the usual manner,³ but now as a function of the sample potential which was varied with respect to a grounded reference electrode. The experiments were carried out for samples of n - and p -type silicon in different crystallographic orientations, and for evaporated silver samples, using different polarizations of both the incident fundamental and the second-harmonic

ic light. The nature of the electrolyte solution and the frequency of the incident light were also varied by utilizing the stimulated Raman-Stokes light from cyclohexane at 8658 \AA .

In Fig. 1 the results are shown for the $(1, 0, 0)$ -

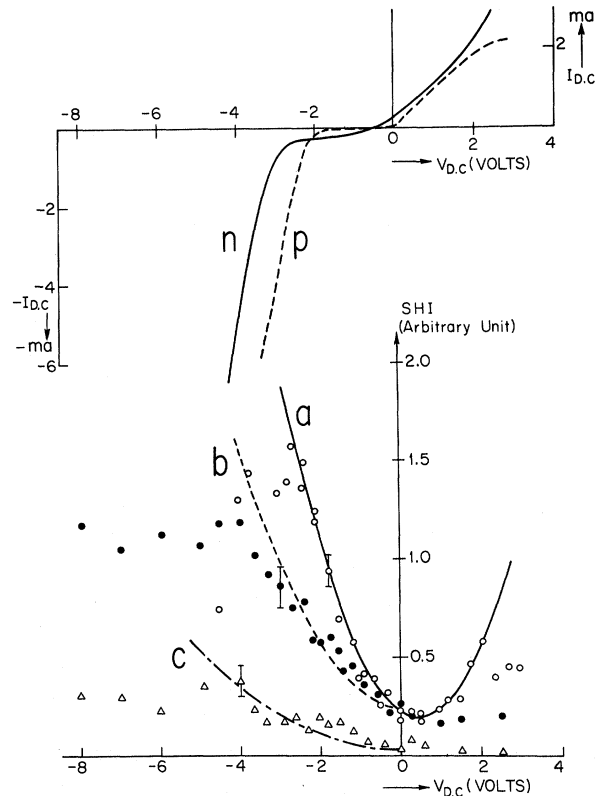


FIG. 1. The second-harmonic intensity from silicon polarized parallel to the plane of incidence for a fundamental wavelength $\lambda = 6943 \text{ \AA}$, as a function of the bias voltage on the sample in a $0.1N$ KCl solution. Curve *a*: The fundamental light is polarized parallel to the plane of incidence on p -type bulk silicon (experimental points, open circles). Curve *b*: Same conditions as *a*, but for a n -type bulk sample (experimental points, solid circles). Curve *c*: The fundamental light is polarized normal to the plane of incidence for n -type bulk silicon (experimental points, triangles). The current-voltage characteristic is shown for the n -type sample (solid line) and for the p -type bulk sample (dashed line).

cut surface of n -type silicon chemically etched by CP4 solution with a bulk resistivity $<100 \Omega \text{ cm}$. The current-voltage characteristic is also shown. For negative bias of the sample a barrier layer is formed. For positive bias electrochemical reactions occur. The second-harmonic beam was polarized in the plane of incidence. The fundamental polarization at 6943 \AA was in the plane of incidence for curve b and perpendicular to this plane for curve c .

Curve a is for a p -type bulk sample. The variation of the second-harmonic intensity with V_{app} is different, especially for positive V_{app} . A qualitative explanation is that the p -type bulk sample has an inversion layer, since the surface of the samples is always n type. The current-voltage characteristic for positive V_{app} is also different.

It is seen that substantial variations in the second-harmonic intensity occur for both polarizations. The intensity is a quadratic function of the applied voltage in the region where the barrier layer is present. Data at 8658 \AA show essentially the same behavior. This fact and the magnitude of the variation show that the origin of the nonlinear effect has nothing to do with critical points near 3.4 eV in the band structure.⁶⁻¹⁰ The convenient terminology "non-linear electroreflectance" does not imply any similarity with the characteristics of the linear electroreflectance. The electric fields near the interface necessary to maintain equilibrium with the surface states and bias conditions produce a sufficient distortion of the wave functions of all electrons near the interface so that the induced second-harmonic polarization described by the last two terms in Eq. (1) is comparable with the first two terms. Essentially the same results were obtained for a 111-cut surface. The cubic symmetry of the lattice is not revealed in the effect, which displayed the same symmetry as an isotropic polycrystalline sample. Changing the electrolyte to a $0.1N$ KOH solution made no difference. For a $0.1N$ HCl solution the experimental points start to deviate from a parabola for lower negative bias voltage, in qualitative agreement with the variation in current-voltage characteristic.

Similar data for a polycrystalline evaporated silver film are shown in Fig. 2. For positive bias of the sample electrochemical reactions occur. For a negative bias the second-harmonic intensity again changes quadratically with the applied voltage, until breakdown

of the barrier layer occurs, as indicated by the current-voltage characteristic. The effect in Ag displays a marked dispersion, as illustrated by curves a and b , for $\lambda = 8658 \text{ \AA}$ and $\lambda = 6943 \text{ \AA}$, respectively. Curve c is for the fundamental field at $\lambda = 6943 \text{ \AA}$ polarized perpendicular to the plane of incidence. It is evident how much the ratio for the second-harmonic intensities for the parallel and perpendicular fundamental polarization depends on the electric field in the surface layer. Such a field may even exist in the unbiased samples in air. This reconfirms our earlier statement³ that extreme care should be exercised in basing conclusions on this experimental ratio.

The electric-field-induced nonlinear polarization is of the same order of magnitude as,

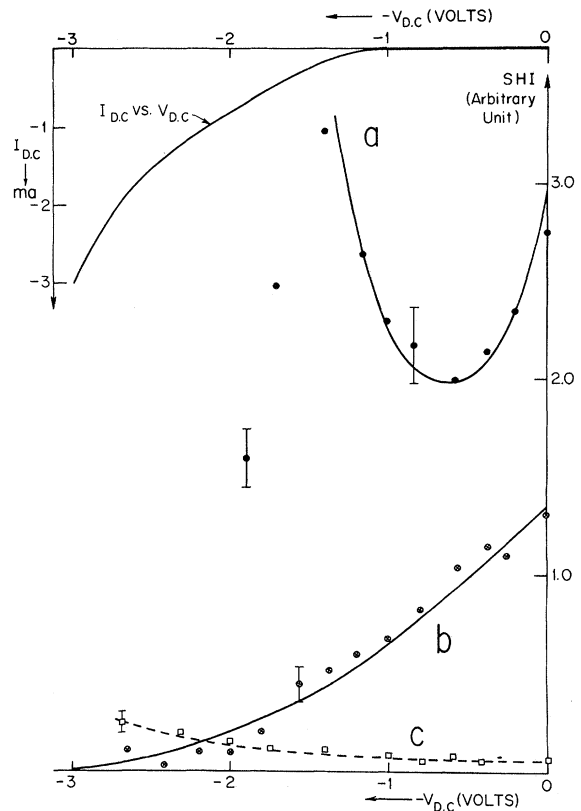


FIG. 2. The second-harmonic intensity from silver, polarized parallel to the plane of incidence, as a function of the bias voltage on the sample in a $0.1N$ KCl solution. The current-voltage characteristic is shown. Curve a : The fundamental light at $\lambda = 8658 \text{ \AA}$ is polarized parallel to the plane of incidence. Curve b : The fundamental light at $\lambda = 6943 \text{ \AA}$ is polarized parallel to the plane of incidence. Curve c : The fundamental light at $\lambda = 6943 \text{ \AA}$ is polarized normal to the plane of incidence.

and can interfere with, the electric-quadrupole and magnetic-dipole terms considered previously.³ For an isotropic medium one has

$$\vec{P}^{NL}(2\omega) = \alpha \vec{E}_L \times \vec{H}_L + \beta \vec{E}_L (\nabla \cdot \vec{E}_L) + \gamma \vec{E}_{dc} (\vec{E}_L \cdot \vec{E}_L) + \gamma' \vec{E}_L (\vec{E}_{dc} \cdot \vec{E}_L). \quad (1)$$

The reflected field generated by the various distributions of harmonic polarization can be calculated by the general methods of Bloembergen and Pershan.¹¹ For a nonabsorbing medium, the fields due to the first two terms in Eq. (1) are 90° out of phase with the field created by the last two terms. The minimum intensity should therefore occur for $E_{dc} = 0$. This is approximately true for experimental results in calcite, but the origin of a well-established small discrepancy has not yet received a satisfactory explanation.^{4,5} In absorbing media, interference is possible because the polarizations of the first-two and the last-two terms in Eq. (1) need not be 90° out of phase. For absorbing media, not only the linear susceptibilities but also the nonlinear coefficients are complex numbers. This may account qualitatively for the observed behavior in silver. In this metal, however, E_{dc} will vary so rapidly in the Fermi-Dirac screening length that terms with $\partial E_{dc}/\partial z$ cannot be ignored. Quantitative knowledge of surface-state wave functions would be required to construct a theory for comparison with the data in Fig. 2.

The results for silicon can be described phenomenologically by Eq. (1). Denote the direction normal to the surface by \hat{z} and the normal to the plane of incidence by \hat{y} . Then $E_{dc} = E_{dc}(z)\hat{z}$, where $E_{dc}(z)$ is determined by a self-consistent field calculation in the Helmholtz and the space-charge layers,¹² while $\Delta \cdot E_L = \partial E_z/\partial z$ is a δ function at the surface. For E_L in the plane of incidence, one has contributions from the last three terms of Eq. (1). For E_L in the y direction, there are contributions only from the first and the third term.

If E_L makes an angle φ with the plane of incidence, the field-induced harmonic polarization will have a component normal to the plane of incidence:

$$P_y(2\omega) = \gamma' E_z(\omega) E_y(\omega) E_{dc} \propto \sin 2\varphi. \quad (2)$$

The field-induced harmonic intensity with this polarization, proportional to $E_{dc}^2 \sin^2 2\varphi$, has been observed experimentally.

In semiconductors one should distinguish between the case where the dc-field penetration depth is less than the optical-absorption depth, or greater. The last situation applies probably in GaAs, which has a Schottky depletion layer⁹ of 10^{-5} to 10^{-4} cm from the surface. In this case the electric field in the optical-absorption depth is rather weak. No variation of harmonic intensity with applied voltage was observed in a GaAs sample, oriented in such a manner that E_L is parallel to 1, 0, 0 axis, to eliminate the large volume harmonic polarization of the piezoelectric crystal.

Because of the nature of the silicon surface states, the dc electric field is perhaps confined to a region smaller than the optical absorption depth d at the harmonic frequency. In this case one may integrate the volume polarization of the last two terms in Eq. (1) to yield an effective surface term proportional to

$$\int_0^d E_{dc} dz = V_{app} + \varphi_s.$$

The parabolic behavior of the intensity in Fig. 1, with a minimum close to $V_{app} = 0$, suggests that the internal surface potential¹² φ_s is small, and that the last two terms are nearly 90° out of phase with the first two terms. It is also possible that the contribution from the internal self-consistent potential φ_s is compensated by the nonlinearity of a surface layer with optical properties different from the bulk. This layer may consist of silicon surface states or adsorbed layers of a different chemical constitution. If the normal to the surface is denoted by \hat{z} , this would lead to the following additional terms, where the superscript (s) denotes a surface layer:

$$\begin{aligned} P_z^{(s)}(2\omega) &= \chi_{zzz}^{(s)} E_z^2 + \chi_{zzx}^{(s)} (E_x^2 + E_y^2), \\ P_x^{(s)}(2\omega) &= \chi_{xxz}^{(s)} E_x E_z, \\ P_y^{(s)}(2\omega) &= \chi_{yyz}^{(s)} E_y E_z. \end{aligned} \quad (3)$$

It will be difficult to determine which value of E_z should be taken in the surface layer. The nonlinearity of SiO₂ or AgO is very small compared with the nonlinearity of Si and Ag, in agreement with Miller's rule that the nonlinearity is a strong function of the linear dielectric constant.¹³ For this reason the nonlinear dipole moment of adsorbed layers is prob-

ably negligible. This is in agreement with the experimental fact that a change in ambient does not change the harmonic-light production, except insofar as it changes the electric field inside the sample. Clearly, further experimentation with better defined and controlled surfaces would be desirable.

The second-harmonic generation of light may provide a new tool for the investigation of surface phenomena. In particular, the nonlinear electroreflectance may prove useful to the study of semiconductor-electrolyte and metal-electrolyte interface properties.

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EXISTENCE OF HYPERBOLIC EXCITONS*

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Calculations based on a band model and interaction appropriate to crystalline Xe are reported which explicitly exhibit narrow peaks interpreted as resonances derived from saddle-point edges, as well as bound states in the energy gap. The results strongly support Phillips's explanation of resonant structure in the optical spectrum of Xe.

Two models have been proposed for the resonant structure frequently observed in the optical spectra of insulators above the direct absorption threshold. The first model^{1,2} attributes the resonances to localized ("molecular") electron-hole excitations, and discusses the positions and multiplicities of the resonances by reference to atomic energy levels and the crystal point group (the group of $\vec{k} = \Gamma = 0$). Phillips^{3,4} has proposed a second model which regards the resonances primarily as kinematic rather than atomic in origin and stresses their Wannier wave-packet character, which is strongly dependent on the crystalline energy bands. He suggests that resonances may be generated not only by thresholds but also by saddle-point edges in the electron-hole joint density of states; such edges usually arise from points \vec{k} on Brillouin zone faces rather than at $\vec{k} = 0$.

Duke and Segall⁵ and Velický and Sak⁶ have studied an effective-mass model of saddle-point edges which does not contain such hyperbolic excitons. The former authors conclude that the essential physics of resonances associated with M_1 edges is best described in terms of localized excitations. We remark that the dispersion relation used by the above authors is characterized by energy surfaces $\epsilon(\vec{k}) = \text{const}$ that are hyperboloids of revolution about the negative mass axis (we assume $m_1 = m_2 > 0$). Consequently, any two energy surfaces $S(E)$, $S(E + \Delta)$ enclose an infinite volume of momentum space, for arbitrarily small Δ (contrast the parabolic effective-mass model, which does not contain this divergence). In this model a "bare" resonance Ψ_0 can be defined with energy $E_{r0} < E_0$, the saddle-point energy, by constructing a wave packet of band states having $\epsilon(\vec{k}) > E_0$ and minimizing the total energy. How-