

## Resonant surface second-harmonic generation: Surface states on Ag(110)

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Frequency-dependent studies of second-harmonic generation from Ag(110) show resonant enhancement due to a transition between two surface electronic states. An increase in the nonlinear susceptibility, attributed to the coupling of the fundamental light with this transition, is proven by the energy dependence of the second-harmonic signal and by the observed selection rules dictated by the symmetry of the surface states.

Second-order nonlinear optical processes such as second-harmonic generation (SHG) are very useful probes for surface and interface structure and phenomena.<sup>1,2</sup> SHG offers excellent time, spatial, and energy resolution, and can be used in a variety of environments, making it a uniquely versatile probe of surface and interface properties. However, very few SHG studies have taken advantage of the energy resolution available from SHG. This work presents frequency-dependent SHG studies, and demonstrates the advantages of such studies in facilitating interpretation of experimental observations that are extremely helpful in furthering our understanding of the SHG process from interfaces. This understanding is necessary in order to take full advantage of the capabilities of SHG. Significant progress toward this goal has been made theoretically and experimentally for simple metals using a "jellium" model for the electrons.<sup>3-5</sup> In these simple metal systems there are resonant processes occurring in the nonlinear optical process, but they are a result of collective excitations at the surface. In contrast to simple metals, the properties of "real" surfaces and interfaces are usually dominated by single-particle surface or interface states. For these systems a conceptual understanding of the relative importance of various sources contributing to SHG is still lacking.

In centrosymmetric media there is no second-order optical response in the dipole approximation, but at a surface or interface, where the inversion symmetry is broken, the nonlinear susceptibility is nonvanishing in this approximation. Thus a strong SHG signal is generated at the interface.<sup>1,2</sup> Because of this surface sensitivity, SHG should be strongly influenced by electronic properties lo-

calized at the interface, i.e., surface or interface states. On the other hand, quadrupole and other higher-order terms may contribute to a bulk SHG response which may interfere with the surface response. Both the magnitude and phase of the bulk response relative to the surface response are unknown, and the two responses cannot be easily distinguished.<sup>6,7</sup> The surface projected band structure shows the possibility of electronic transitions which are distinctly different, in both energy and symmetry properties, from those possible in the bulk. SHG can be enhanced by resonances with electronic transitions both in the bulk and at the surface. These resonances can be manifested through different physical parameters, namely the nonlinear susceptibility and the dielectric constants.

The dielectric response, i.e., the Fresnel factors, describes the propagation of optical fields at both  $\omega$  and  $2\omega$  in the substrate and at the interface. The nonlinear susceptibility generates the nonlinear response of the material to the incident electric field. Both of these parameters are composed of contributions from individual electronic transitions in the material. The dielectric properties are conventionally measured using linear optical techniques which are not surface sensitive; therefore the Fresnel factors include the effects of bulk electronic properties, but not surface properties. In contrast,  $\chi^{(2)}$ , the dipole part of the nonlinear response, is particularly sensitive to surface electronic properties. Therefore nonlinear studies are particularly useful for characterization of these interfacial states.<sup>8,9</sup>

The relationship between  $\chi^{(2)}$  and the electronic band structure can be described in a single-particle excitation picture by the following equation:

$$\chi_{ijk}(2\omega; \omega, \omega) = -Ne^3 \sum_{(a,b,c)} \frac{\langle a|r_i|c\rangle \langle c|r_j|b\rangle \langle b|r_k|a\rangle}{(2\hbar\omega - E_{ca} - i\hbar\gamma_{ca})(\hbar\omega - E_{ba} - i\hbar\gamma_{ba})}, \quad (1)$$

where  $r_i$  is the Cartesian coordinate operator, and  $|a\rangle$ ,  $|b\rangle$ , and  $|c\rangle$  represent the initial, intermediate, and final state, respectively. The other symbols have their conventional meanings. It is evident that if either  $\hbar\omega$  or  $2\hbar\omega$  is near the energy of a transition between two single particle

states,  $\chi^{(2)}$  will be resonantly enhanced. The matrix elements in the numerator determine how the optical field is coupled to the transition in terms of symmetry selection rules. Resonance enhancement in SHG can thus be used as a sensitive probe for specific electronic resonances at

an interface. Several groups have proposed that surface states have influenced their SHG results,<sup>8–13</sup> but unambiguous evidence of the surface-state contribution has not been demonstrated, either because detailed frequency-dependent studies were not done or because the electronic properties of the system remain in question.<sup>8,14</sup> This paper presents clear evidence of a surface-state resonance in  $\chi^{(2)}$ .

SHG as a function of incident energy, polarization, and crystal orientation from a Ag(110) surface has been studied as a test case for our understanding of resonant surface second-harmonic generation. This surface was chosen because the occupied and unoccupied surface states have been measured<sup>15–17</sup> and calculated.<sup>18</sup> The detailed knowledge of both the surface and bulk electronic properties facilitates interpretation of the SHG results and allows us to easily identify various contributions to the nonlinear optical response.

The experiments were performed in an ultrahigh vacuum chamber with a base pressure of  $5 \times 10^{-11}$  Torr. Before each experiment the crystal was cleaned by a brief sputter and anneal. The laser pulses were supplied by a pulsed dye laser (Spectra-Physics PDL-2) pumped by a 10-Hz Nd:YAG (where YAG denotes yttrium aluminum garnet) laser (Quantel 581C), rendering a tuning range of about 580 (2.14 eV) to 900 nm (1.38 eV) with 10-ns pulses and 20–100 MW/cm<sup>2</sup> peak power. Light was directed onto the crystal at 60° angle of incidence. Only *p*-polarized SHG was detected, as verified by a polarizer placed after the chamber. A fraction of the laser light was split off from the beam and directed onto a potassium dihydrogen phosphate (KDP) crystal. SHG reflected from the KDP crystal,  $I_{2\omega, \text{ref}}$ , was used as a reference to correct for laser intensity fluctuations.  $I_{2\omega, \text{ref}}$  is independent of laser polarization and crystal orientation. Calibration for different laser energies was accomplished both through the KDP reference signal and overlap of adjacent dye wavelengths.

The SHG spectra obtained for two different planes of incidence are shown in Fig. 1. In both parts the signal due to *p*-polarized incident light is indicated by the solid squares, while the *s*-polarized incident signal is shown by the circles. The incident plane in Fig. 1(a) is parallel to the  $[1\bar{1}0]$  direction while the crystal has been rotated in Fig. 1(b) so that the plane of incidence is parallel to the  $[001]$  direction.

We have shown that peak *A* is due to the Ag interband transitions at  $2\hbar\omega = 3.8\text{--}4.0$  eV.<sup>19,20</sup> In this energy region, the dielectric constant displays a sharp frequency dependence. Both the real and imaginary parts of the dielectric constant are close to zero near 3.8 eV. Thus an enhancement of the electric fields in the metal due to the presence of interband transitions results in strong SHG radiated at the surface.

Peak *B* in these spectra can be assigned to a resonance in  $\hbar\omega$  with a transition from an occupied surface state to an unoccupied surface state. Surface states have been found in gaps at the  $\bar{Y}$  and  $\bar{X}$  zone boundaries of the Ag(110) surface Brillouin zone,<sup>15–18</sup> Fig. 2(a). The state at  $\bar{X}$  is approximately 5 eV above the Fermi level and is too high in energy to be involved in a resonant excitation

with the laser frequencies used in these studies. On the other hand, the states at  $\bar{Y}$  have exactly the correct energy. The occupied surface state has been observed experimentally; it lies less than 0.1 eV below the Fermi energy at the zone boundary.<sup>15</sup> The unoccupied surface state near  $\bar{Y}$  has been predicted theoretically<sup>18</sup> and observed in inverse photoemission experiments, and is approximately 1.65 eV above the Fermi energy.<sup>16,17</sup> This upper state has the same *s*-orbital symmetry as the states which make up the top of the band gap.<sup>18</sup> The lower, occupied state, is split off from states of *p*-orbital symmetry which make up the bottom of the band gap at  $\bar{Y}$ ,<sup>18</sup> and this surface state has the same symmetry as those states. If the transition between the two surface states is coupled to the fundamental light in the SHG process, there should be a dramatic polarization dependence of the SHG signal depending upon the crystal orientation, as predicted by the symmetry properties of the states as included in the matrix elements of Eq. (1).

The matrix element for excitation between these two states is the familiar photoexcitation matrix element  $\langle \Psi_i | \mathbf{A} \cdot \mathbf{P} | \Psi_f \rangle$ . The form of the matrix elements in Eq. (1), using the Cartesian coordinate operator, is derived

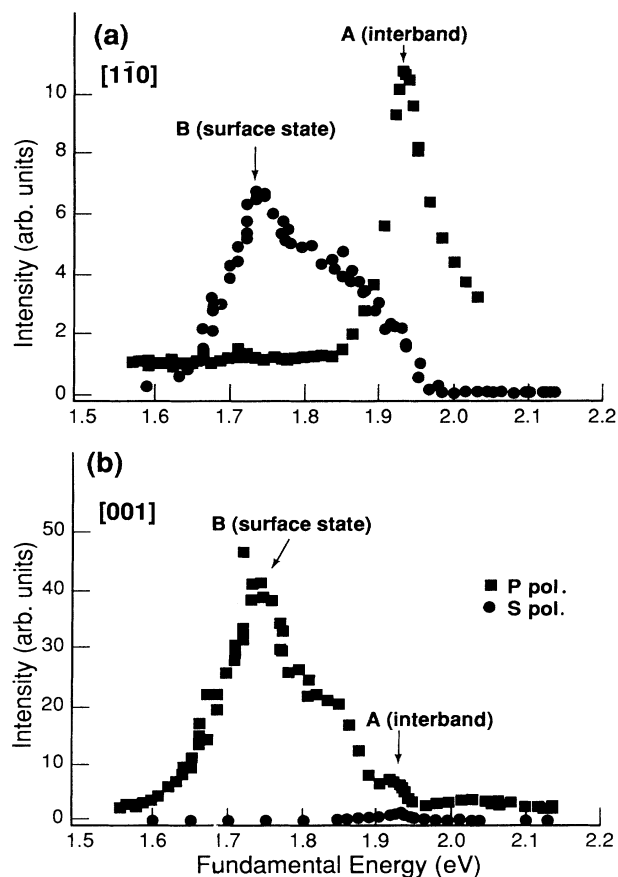


FIG. 1. SHG as a function of fundamental energy. The squares represent *p*-polarized incident light, the circles *s*-polarized incident light. (a) The plane of incidence is parallel to  $[1\bar{1}0]$ . (b) This plane of incidence is parallel to  $[001]$ . The units in (a) and (b) are arbitrary but of the same magnitude, and have been divided by  $I_{2\omega, \text{ref}}$ .

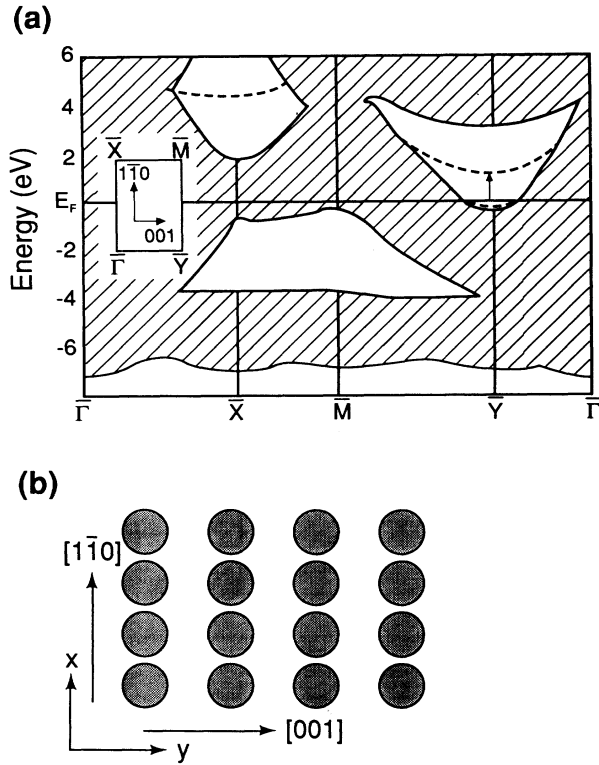


FIG. 2. (a) Surface projected band structure adapted from Ref. 18. Surface states are represented by dashed lines. One quarter of the surface Brillouin zone is shown in the inset. (b) Orientation of  $x$ - $y$  plane with respect to crystal axes.

from this matrix element after several approximations.<sup>21</sup> The selection rules which define the necessary orientation of the incident light polarization with respect to the crystal axes in order to excite a transition between the surface states can be derived in a straightforward manner by considering the symmetry of the surface states in coordinate space.

Let the  $x$ - $y$  plane be fixed to the crystal surface, with the  $x$  axis parallel to the  $[1\bar{1}0]$  direction and the  $y$  axis parallel to the  $[001]$  direction, as shown in Fig. 2(b). The  $z$  axis is normal to the crystal surface. The upper  $s$ -like state is symmetric with respect to reflection about both the  $x$ - $z$  and the  $y$ - $z$  planes. The lower state is even about the  $y$ - $z$  plane, but odd about the  $x$ - $z$  plane.<sup>18</sup> Since both wave functions for the surface states are even in the  $y$ - $z$  plane,  $\mathbf{A} \cdot \mathbf{P}$  must also be even in this plane.  $\mathbf{A} \cdot \mathbf{P}$  must be odd about  $x$ - $z$  plane since the initial state is odd and the final state is even about this plane. These conditions require that a component of the incident light polarization must be parallel to the  $[001]$  direction ( $\hat{y}$ ) for a nonzero matrix element. This requirement has been derived by Ho, Harmon, and Liu<sup>18</sup> from pseudopotential calculations, and demonstrated by Boeck and Kolb<sup>22</sup> in linear electroreflectance studies. For the geometry shown in Fig. 1(a), with the plane of incidence parallel to the  $[1\bar{1}0]$  direction (i.e., in the  $x$ - $z$  plane), this criterion is satisfied for  $s$ -polarized incident light, which is perpendicular to the plane of incidence. A strong peak centered at 1.74 eV is clearly evident in this figure for  $s$ -polarized incident

light. In contrast, the signal with  $p$ -polarized incident light shows no frequency dependence in this energy range. Consider next what happens when the crystal is rotated  $90^\circ$  so that the incident plane is parallel to the  $[001]$  direction (the  $y$ - $z$  plane), as shown in Fig. 1(b). In this geometry,  $p$ -polarized incident light has a component of its polarization parallel to the  $[001]$  direction, while  $s$ -polarized light is completely orthogonal to this direction. It is clear from the data shown in Fig. 1(b) that in this configuration,  $p$ -polarized incident light couples to the transition between the two surface states, resulting in a resonant enhancement in SHG, while the signal due to  $s$ -polarized incident light is below the detection limit.

The relative strength of  $I_{2\omega}$  at the surface state resonance for  $p$ - and  $s$ -polarized incident light can be explained by considering the relative magnitudes of the electric fields in the metal at the surface for the two different incident polarizations. In this case there are two  $\chi^{(2)}$  elements which contain a  $y$  component and therefore can couple the two surface states and are primarily responsible for SHG at 1.74 eV:  $\chi_{zyy}$  and  $\chi_{yzy}$ . The measured SHG signal is proportional to  $|\chi_{ijk} E_j E_k|^2$ . The magnitude of  $E_y$  and  $E_z$  can be calculated using macroscopic Fresnel equations. In these equations,  $E_z$  appears as the field perpendicular ( $\perp$ ) to the surface, and  $E_y$  parallel ( $\parallel$ ) to the surface. For silver, at  $60^\circ$  angle of incidence and  $p$ -polarized incident light, the ratio of  $E_{\parallel}$  to  $E_{\perp}$  is approximately 6 at  $\hbar\omega = 1.74$  eV.<sup>23</sup> This means that the most important contribution to the SHG signal for this incident polarization comes from  $|\chi_{zyy} E_y^2|^2$ . The parallel component of the electric field inside the metal is actually larger for  $p$ -polarized incident light than for  $s$ -polarized incident light. Again, using the Fresnel equations, the ratio of the contribution from  $\chi_{zyy} E_y^2$  to the SHG signal for the two different polarizations at 1.74 eV can be approximately calculated as

$$\frac{|\chi_{\perp\parallel\parallel} E_{\parallel}^2 (p\text{-pol})|^2}{|\chi_{\perp\parallel\parallel} E_{\parallel}^2 (s\text{-pol})|^2} \approx 13.$$

This estimation is in reasonable agreement with the observed ratio of 7 of  $I_{2\omega}(p\text{-pol})$  to  $I_{2\omega}(s\text{-pol})$ .

The center of the peak at  $1.74 \pm 0.02$  eV agrees very well with the 1.75 eV value deduced from previous measurements of the energies of the two surface states. The peak is highly asymmetric with a full width at half maximum of 0.21 eV. Transitions from bulk states below the band gap, which have the same symmetry as the occupied surface state, to the unoccupied surface state will occur for slightly higher photon energies than those required for the pure surface state transitions. This accounts for the tail in the peak towards the high-energy side.

At 94 K, the resonant signal is rapidly and completely quenched upon exposure to water or oxygen, as is expected for a surface state whose existence is very sensitive to surface conditions. The nonresonant signal at 1.74 eV, however, is not reduced by exposure to water. At 1.72 eV, the nonresonant signal is quenched upon oxygen exposure, but not as rapidly as the resonant signal. Previous experiments have shown that adsorption of oxygen reduces the nonresonant SHG signal at 2.34 eV.<sup>24</sup>

The temperature dependence of the SHG signal from

Ag(110) exhibits very interesting behavior. Both peaks in Fig. 1 drop in intensity as the crystal temperature is raised from 94 to 575 K. The interband peak energy appears to shift to lower energy, quench, and become broader.<sup>20</sup> This behavior is similar to changes in the energy-loss function measured by linear reflection experiments.<sup>25</sup> The temperature dependence of the surface-state peak may be due to both energy shifts and changes in occupation of the lower state as a function of temperature. These effects will be discussed in detail elsewhere.<sup>19</sup> It should be noted that the SHG signal at 1.74 eV with *p*-polarized [1 $\bar{1}$ 0] incident light and with *s*-polarized [001] incident light does not display any temperature dependence.

The importance of frequency-dependent experiments is clear from these results. Had SHG from Ag been studied as a function of incident polarization and plane relative

to the crystal axes, but using only the fundamental (1.17 eV) and the SHG (2.34 eV) output of the Nd:YAG laser, it would not have been possible to identify *either* the resonance of  $\chi^{(2)}$  with the transition between surface states or the effect of the interband transitions on the SHG signal.

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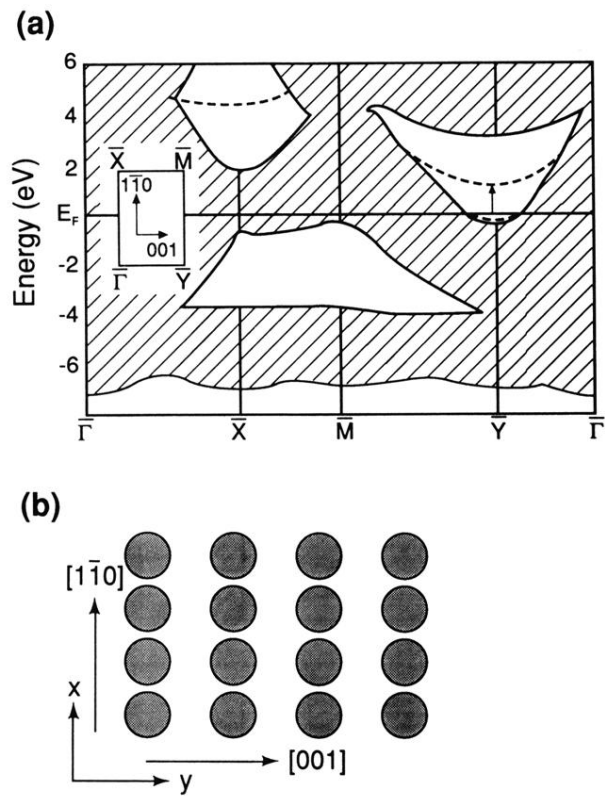


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