Surface-dipole and electric-quadrupole contributions to anisotropic second-harmonic generation from noble-metal surfaces

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The azimuthal anisotropy in the optical second-harmonic response from various crystal faces of Ag, Cu, and Au has been measured. Comparing the relative magnitude of the isotropic and anisotropic signals indicates that the strong anisotropy observed from the (111) and (110) faces of noble metals can be assigned primarily to the dipolar surface response. This result contrasts to the case of Al single crystals where the anisotropy can be accounted for by the bulk quadrupole response.

I. INTRODUCTION

Second-harmonic generation (SHG) is a versatile technique for studying a variety of interfaces *in situ*.[1] Fundamental to the application of the technique to problems in surface science is the constraint of the local dipolar response to the surface region between two centrosymmetric media, which lends SHG its surface specificity. In addition to the dipolar surface response, there are higher-order responses due to gradients in the fields and the susceptibilities which can lead to a SH signal determined by properties of the bulk medium. Since in most cases a separation of these bulk contributions from surface effects is not possible experimentally, a knowledge of their relative magnitudes is highly desirable. Without at least a qualitative measure of their relative magnitudes, an unambiguous interpretation of many experimental effects is precluded.

The bulk anisotropic response due to gradients in the incident fields can be isolated at the (100) and (110) face of a single crystal and the relative magnitude of this contribution to the SH production evaluated. These signals have been measured here for noble-metal surfaces and compared to the anisotropic response observed where both bulk and surface terms are present. The results on Au(100), Ag(100), and Cu(100) in air and immersed in aqueous electrolytes demonstrate that the nonlocal anisotropic response due to field gradients is significantly less for these surfaces than that previously reported for Al(100).[2] This bulk response is also determined to be more than an order of magnitude smaller than the corresponding surface terms for the Ag(110) surface. Comparison of the (100) and (111) results shows that the surface contribution to the (111) response is larger than that from the quadrupole term for noble metals.

II. THEORY

The nonlinear polarization induced in a medium that is responsible for the radiation at the second-harmonic frequency (2ω) is given by

$$P_i(2\omega) = \chi_{ijk}^{(2)D} E_j(\omega) E_k(\omega) + \chi_{ijk}^{(2)S} E_j(\omega) E_k(\omega)$$
$$+ \chi^{(2)} Q_{ijkl} E_j(\omega) \nabla_k E_l(\omega) . \qquad (1)$$

The first term on the right-hand side of Eq. (1) corresponds to the dipolar bulk response which vanishes in the bulk of centrosymmetric media. The second term is the surface-dipole term derived from the breakage of inversion symmetry at the boundary.[3] The third term is the electric-quadrupole response. As noted by Guyot-Sionnest and Shen,[4] an additional contribution not appearing in Eq. (1) can be derived if one considers the abrupt variation of the quadrupole susceptibility at the surface.[5]

Expressions for the SH response from cubic media as a function of crystal orientation have been developed by Tom[6] and codified by others.[7,8] For the (100) or (111) crystal face the SH intensity assumes the form

$$I_{p,p}(2\omega) = |a_{p,p}^{(0)} + a_{p,p}^{(m)} \cos(m\phi)|^2 , \qquad (2)$$

$$I_{p,s}(2\omega) = |a_{p,s}^{(m)} \sin(m\phi)|^2 , \qquad (3)$$

$$I_{s,p}(2\omega) = |a_{s,p}^{(0)} + a_{s,p}^{(m)} \cos(m\phi)|^2 , \qquad (4)$$

$$I_{s,s}(2\omega) = |a_{s,s}^{(m)} \sin(m\phi)|^2 , \qquad (5)$$

where the azimuthal angle ϕ, describing the rotation of the crystal about its surface normal, is the angle between the [0$\bar{1}$0] ([2$\bar{1}$$\bar{1}$]) crystal axis and the projection of the wave-vector $\mathbf{k}(\lambda)$ on the surface with $m = 4(3)$ for the (100) [(111)] crystal face. The subscripts refer to the (fundamental, second-harmonic) beam polarizations, either in the plane of incidence (p polarized) or perpendicular (s polarized) to it.

Explicit expressions for the rotational constants $a_{i,j}^{(m)}$ are given in Ref. 7. In general, both $\chi^{(2)S}$ and $\chi^{(2)Q}$ contribute to the anisotropy of the second-harmonic radiation. For the (100) face, however, the only contribution to the anisotropy $a_{i,j}^{(4)}$ is $\zeta \equiv \chi_{1111}^{(2)Q} - (\chi_{1122}^{(2)Q} + \chi_{1212}^{(2)Q} + \chi_{1221}^{(2)Q})$.

The term ζ can also be isolated as the anisotropic response from a (110) surface if the appropriate polarizations of incoming and outgoing fields are selected. For the (110) face the SH intensity can be described as[6]

$$I(2\omega)_{p,p} = |a_{p,p}^{(0)} + a_{p,p}^{(2)} \cos(2\phi) + a_{p,p}^{(4)} \cos(4\phi)|^2 , \qquad (6)$$

$$I(2\omega)_{p,s} = |a_{p,s}^{(2)} \sin(2\phi) + a_{p,s}^{(4)} \sin(4\phi)|^2 , \qquad (7)$$

$$I(2\omega)_{s,p} = |a_{s,p}^{(0)} + a_{s,p}^{(2)} \cos(2\phi) + a_{s,p}^{(4)} \cos(4\phi)|^2 , \qquad (8)$$

$$I(2\omega)_{s,s} = |a_{s,s}^{(4)} \sin(4\phi)|^2 , \qquad (9)$$

where ϕ is the angle between the projection of $\mathbf{k}(\lambda)$ on the surface and the [110] crystal direction. The anisotropic terms $a_{i,j}^{(2)}$ contain a contribution from surface-dipole terms as well as the electric-quadrupole response ζ. The fourfold anisotropy $a_{i,j}^{(4)}$ is derived solely from the quadrupole term ζ.

III. EXPERIMENT

The experimental apparatus and procedures have been described in detail elsewhere.[9] The single-cyrstal electrodes are mechanically polished using diamond paste down to 0.25 μm. Electrochemical or chemical polishing was then used to remove the plastically deformed surface layer. The electrochemical polishing and transfer of the silver and copper electrodes to the spectroelectrochemical cell was done under an inert atmosphere to minimize oxide formation. Following the electropolishing of gold, the electrodes were subjected to a flame treatment.[10] Electrochemical polishing of Al was not necessary to observe an appreciable anisotropic response. Experiments on Ag, Cu, and Au were performed both at the metal-electrolyte interface under potential control and at the metal-air interface. The excitation wavelength for these experiments, $\lambda = 1.06$ μm, is the fundamental of a Nd:YAG (yttrium aluminum garnet) laser operating at 10 Hz. The fundamental beam, collimated to a diameter of 2.0 mm, is incident upon the sample at an angle $\theta_{in} = 32°$ with an energy density of 1–6 mJ/cm^2.

IV. RESULTS AND DISCUSSION

As described in Sec. II, there is no surface-dipolar contribution to the anisotropic SH response from the (100) face of a cubic crystal. Therefore, any anisotropy observed in the second-harmonic signal in this case is due to the quadrupole response ζ. This bulk anisotropic response has been previously observed for the cubic semiconductors Si(100) (Refs. 11 and 12) and Ge(100),[13] as well as for Al(100).[2] Figure 1 shows the p-polarized SH signal from Al(100) using p- and s-polarized excitations. The crystal surface was prepared by polishing with diamond paste down to 0.25 μm. A pronounced fourfold symmetry is observed in the rotational anisotropy, indicating a significant contribution from ζ to the response. The solid lines in the figure are fit to the data using Eqs. (2) and (4) setting values of $a_{p,p}^{(0)}/a_{p,p}^{(4)} = 6.2$ and $a_{s,p}^{(0)}/a_{s,p}^{(4)} = 2.0$. In Ref. 2, values of $a_{p,p}^{(0)}/a_{p,p}^{(4)} = 3.3$ and $a_{s,p}^{(0)}/a_{s,p}^{(4)} = 2.5$ were obtained from the Al(100)-air interface. This relatively small difference in the measured values of $a^{(0)}/a^{(4)}$ is not surprising given the fact that the surfaces were only mechanically polished and some oxidation of the aluminum surface will take place.

The bulk anisotropy observed from (100) crystals of the noble metals is much weaker than in the case of Al(100). Figures 2–4 show the results for the (100) crystals of Ag, Au, and Cu, respectively, after removing the plastically deformed surface layer by electrochemical polishing. Only a slight modulation in the $I_{p,p}(\phi)$ signal is observed for any of the crystals examined. A fit to the data using Eq. (2) yields a lower limit on the value $a_{p,p}^{(0)}/a_{p,p}^{(4)}$ and the

results are given in the figure captions. Similar results were obtained for each crystal when immersed in an electrolyte and held at the potential of zero charge. For the signal shown in Fig. 3 from Au(100), a periodic response was difficult to discern or fit to Eq. (2). We found the best fit to require an additional cos(ϕ) term be added to Eq. (2). This effect could be due to a beam walk as the crystal is rotated or to intensity variations due to sampling different regions of the crystal surface.

A strategy for explicitly separating the surface and bulk responses for the (111) surface involves measuring the relative intensity of the s-polarized SH from the (100) crystal using a p-polarized excitation and comparing it to the relative intensity of the same signal from the (111) face.[9] The s-polarized SH from the (100) face yields a value for $|a\zeta|$, whereas the s-polarized (111) response is a measure of $|b\zeta + c\chi_{xxx}|$, where a, b, and c represent local-field corrections (Fresnel factors).[13] The relative magnitude of the surface to bulk susceptibility is then given by

$$\sqrt{\rho}|a/c| - |b/c| \le |\chi_{xxx}/\zeta| \le \sqrt{\rho}|a/c| + b/c| , \qquad (10)$$

where $\rho \equiv (I_{p,s}^{(111)}/I_{p,s}^{(100)})$ and the range of values accounts for possible phase differences between χ_{xxx} and ζ. In this manner, Tom, Heinz, and Shen[11] were able to determine
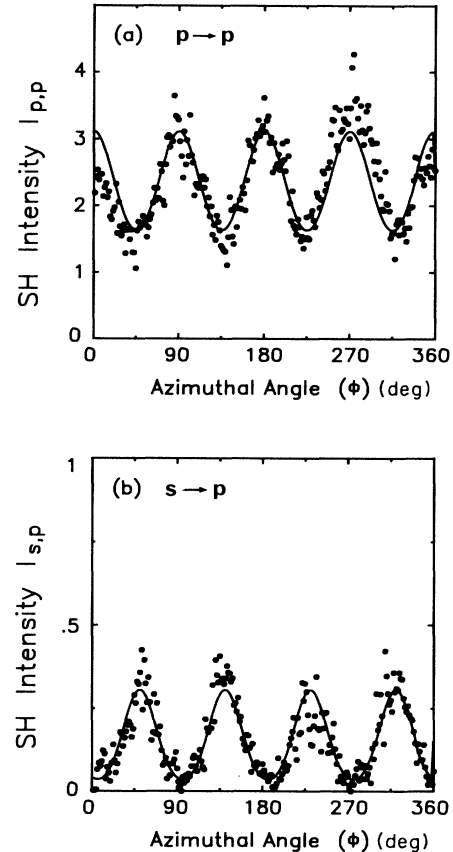

FIG. 1. p-polarized second-harmonic intensity from the Al(100)/air interface as a function of the azimuthal angle ϕ. The solid lines are fits to Eqs. (2) and (4). (a) p-polarized excitation, $a_{p,p}^{(0)}/a_{p,p}^{(4)} = 6.2$; (b) s-polarized excitation, $a_{s,p}^{(0)}/a_{s,p}^{(4)} = 2.0$.
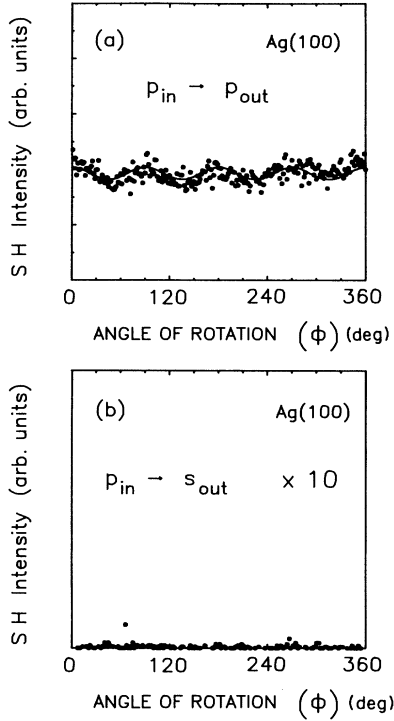
FIG. 2. Second-harmonic intensity from the Ag(100)-air interface as a function of the azimuthal angle ϕ. Excitation beam is p-polarized. (a) p-polarized SH. The solid line is fit to Eq. (2) setting $a_{p,p}^{(4)}/a_{p,p}^{(0)}=0.03$; (b) s-polarized SH.

that the bulk and surface terms of silicon made comparable contributions to the anisotropy.

Similar measurements were conducted in this laboratory on the (111) and (100) faces of the noble metals. We were not able to measure values of ρ greater than 2×10^2 for Au, Ag, or Cu due to an isotropic background signal in the $I_{p,s}(100)$ data from the metal surfaces. As a result, we are only able to set a limit on the magnitude of the quadrupole term relative to the surface-dipole contribution. For example, a value of $|\chi_{xxx}/\zeta|>0.041$ was obtained for Au by estimating the magnitude of an anisotropic signal that might be buried within the isotropic background observed in the s-polarized (100) response.
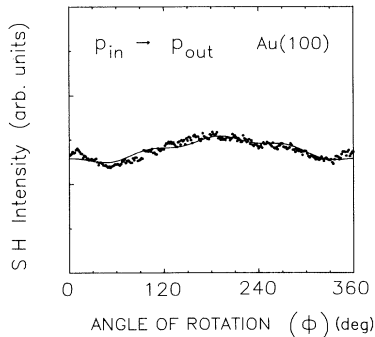

FIG. 3. SH intensity $I_{p,p}$ from the Au(100)-air interface as a function of angle of rotation ϕ. The solid line is a fit to Eq. (2) setting $a_{p,p}^{(4)}/a_{p,p}^{(0)}=0.01$.
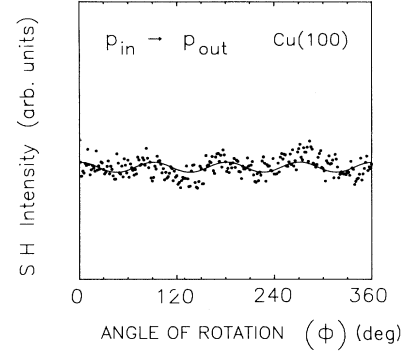

FIG. 4. SH intensity $I_{p,p}$ from the Cu(100)-air interface as a function of angle of rotation ϕ. The solid line is a fit to Eq. (2) setting $a_{p,p}^{(4)}/a_{p,p}^{(0)}=0.03$.

This means that the surface and bulk contributions to the Au(111) signal may be comparable in magnitude for these experiments, given that $|b/c|=0.087$.[14] Since a *direct* measurement of $|a\zeta|$ was not obtained from the s-polarized Au(100) data, these numbers represent an upper limit on the magnitude of $|\zeta|$ relative to $|\chi_{xxx}|$. Other results indicate that the actual value of $|\chi_{xxx}/\zeta|$ is significantly greater than 0.04.

Since the Fresnel coefficients are functions of θ_{in}, one might contemplate varying the incident angle as a means of separating the signal due to ζ from the signal due to $\chi^{(2)S}$. This was first suggested in Ref. 7 where the authors showed that for silicon a similar θ_{in} dependence of the Fresnel coefficients scaling ζ and $\chi^{(2)S}$ prevents such a determination. In the appendix of Ref. 7 we show a similar result holds for noble metals at the wavelengths used here. A further implication of this fact is that the conclusions reached in the following discussions regarding relative contributions of bulk and surface terms to the observed SH intensities are applicable at other values of $\theta_{in}=32°$.

Another means of obtaining the relative strength of the quadrupole term ζ relies on the assumption that the isotropic terms contributing to $I(2\omega)_{p,p}$ are equal in magnitude for the (111) and (100) crystal faces. An examination of the terms contributing to $I(2\omega)_{p,p}$ (see Ref. 7, Table V) reveals that they are identical for the (111) and (100) surfaces except for the Fresnel factors scaling the contribution from ζ. To test the validity of this assumption, we measured $I_{p,p}^{(100)}/I_{p,p}^{(111)}$ at azimuthal angles where the anisotropic contributions vanish and obtained a value of 0.98 for Au. Since the assumption appears valid in the case of the noble metals [as was found for Si (Ref. 15)], a fit to the data $I_{p,p}^{(100)}(\phi)$ and $I_{p,p}^{(111)}(\phi)$ results in a value of $|a_{p,p}^{(4)}/a_{p,p}^{(3)}|$ that can be used to determine $|\chi_{xxx}/\zeta|$. For Au, a value of $0.86 \leq |\chi_{xxx}/\zeta| \leq 0.87$ is obtained. This result implies that the relative surface-dipole-to-quadrupole contribution for the p-polarized Au(111) anisotropy at an incident angle of $\theta_{in}=32°$ is $|c\chi_{xxx}| \approx 10|b\zeta|$. A similar analysis for the p-polarized signals from Ag(100) and Ag(111) results in a value of $|c\chi_{xxx}| \approx 3|b\zeta|$. In the case of copper we obtained a value of $|c\chi_{xxx}| \approx 4|b\zeta|$. We note that due to the
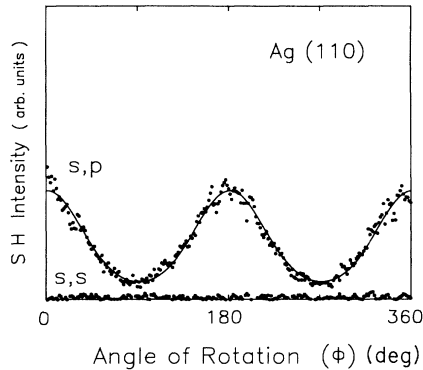
FIG. 5. SH intensity from Ag(110) as a function of angle of rotation ϕ. The solid line is a fit to Eq. (8) (see text). The electrode was immersed in 0.25 M Na_2SO_4, $E = -0.69$ V (vs Ag/AgCl).

significant amount of noise (relative to the magnitude of the anisotropy) in the $I_{p,p}$ data, these results are likely an overestimation of the contribution of ζ to the (111) anisotropy. The (110) results presented below indicate that is indeed the case.

The quadrupole response ζ can also be studied by examining the response of the (110) surface. The s-polarized signal from an s-polarized pump beam is solely derived from the electric-quadrupole response ζ. In the case of Ag(110) we were unable to detect an anisotropic $I_{s,s}^{(110)}$ signal. The rotational anisotropy observed for Ag(110) using a 1.064-μm s-polarized excitation is shown in Fig. 5. The anisotropy seen for the p-polarized SH from the (110) crystal is due to a sum of a dipolar surface response and the quadrupolar anisotropy ζ. The isotropic and anisotropic contributions to $I_{s,p}$ for the (110) crystal are nearly equal in magnitude as indicated by the near-zero minimum observed for $\phi = \pi/2, 3\pi/2$. The data are well fit by Eq. (8) setting $a_{s,p}^{(0)} = 1.0$ (± 0.04), $a_{s,p}^{(2)} = 0.42$ (± 0.03), and $a_{s,p}^{(4)} = 0.005$ (± 0.015). The term a^2 contains contributions from both ζ and $\chi^{(2)s}$. The term $a^{(2)}$ contains only a contribution from ζ. The relative values of $a^{(2)}$ and $a^{(4)}$, along with the lack of signal for $I_{s,s}$, suggest that the contribution of ζ to the Ag(110) anisotropy observed is negligible under these experimental conditions.

A novel method of separating ζ from the surface contribution involves using the ratio $a_{s,p}^{(2)}/a_{s,p}^{(4)}$ obtained in the fit to the data from Fig. 5 to estimate the relative contributions of $|b\zeta + c(\chi_{zxx} - \chi_{zyy})| = a_{s,p}^{(2)}$ and $|a\zeta| = a_{s,p}^{(4)}$. The relative values of the Fresnel factors are $|b/c| = 0.014$ and $|a/c| = 0.004$ and a value of $|(\chi_{zxx} - \chi_{zyy})/\zeta)| \geq 0.62$ (± 0.20) is obtained, where the uncertainty is derived from the fitting parameters. The ratio of susceptibilities indicates a relative contribution in the observed intensity

$I_{s,p}^{(110)}$ of $|c(\chi_{zxx} - \chi_{zyy})/b\zeta| \geq 45.9$ (± 15.2). The relative phase of the susceptibilities is undetermined but the effect of interferences is less than the error introduced by the fits. We note that the electric-quadrupole response from Al(110) (Ref. 16) is much stronger than from Ag(110) at these wavelengths, similar to the results observed at the (100) face of the two metals.

Assuming that the isotropic response from the Ag surface is independent of the crystal face under study, we can use the Ag(110) results to estimate the relative strength of contributions to the Ag(111) anisotropy. A fit of our data to Eq. (4) results in a value of $a_{s,p}^{(3)}/a_{s,p}^{(0)} = -18.5$. Given that $a_{s,p}^{(4)}/a_{s,p}^{(0)} = -0.005$, we find that $|\chi_{xxx}/\zeta| \approx 3.9$. The magnitude of the surface-dipole contribution to the (111) anisotropy relative to the electric-quadrupole contribution is calculated to be $|c\chi_{xxx}/b\zeta| \approx 42$. This result suggests that the comparison of $I_{p,p}(100)$ to $I_{p,p}(111)$ discussed above overestimates the magnitude of ζ.

V. SUMMARY

Noble-metal (100) surfaces show a greatly reduced SH anisotropy compared to the previously reported results from (100) surfaces of Al and semiconductors. By comparing the anisotropy observed from the (111) and (100) faces relative to the isotropic SH response, we have determined that the surface-dipole contribution to the (111) anisotropy is at least 3, 4, and 10 times greater than the quadrupole anisotropy for Ag, Cu, and Au, respectively. Further measurements on the (110) face of Ag have shown that these results may overestimate the strength of the electric-quadrupolar term. For Ag(110), the anisotropy in the SH intensity derived from the surface-dipolar response is at least 30 times that arising from the electric-quadrupole response from that surface. Knowledge of the relative magnitude of the anisotropic terms is important in understanding the effects of surface modification (e.g., adsorption processes) on the SH efficiency of the interfacial region.

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