

## Observation of rotational anisotropy in the second-harmonic generation from a metal surface

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(Received 7 March 1986)

We show that crystalline metal surfaces, in particular the Cu(111) surface, exhibit strong second-harmonic (SH) rotational anisotropy. The form of this anisotropy is fully predicted by the current theory of SH from the surface and near-surface bulk of centrosymmetric media. This SH anisotropy allows measurements of changes in atomic order, e.g., phase transitions, on metal surfaces. Since the anisotropic contribution can only arise from interband transitions, it provides greater SH sensitivity to distinguishing adsorbate binding sites.

Recently, second-harmonic generation (SHG) has been shown to be an extremely sensitive probe of adsorbate-induced changes in the electronic properties of surfaces.<sup>1,2</sup> Information about adsorbate coverage, bonding site, and bonding orientation may be deduced from SHG measurements.<sup>3</sup> SHG has also been shown to reveal structural symmetry of semiconductor surfaces<sup>4,5</sup> and has been used as a measure of surface order during melting.<sup>6</sup> This latter sensitivity to structural order arises from a remarkable anisotropy in the SH signal from a crystalline surface as the surface is rotated about its surface normal. This anisotropy was not detected in earlier works on SH from surfaces,<sup>7</sup> probably because the surfaces lacked sufficient crystalline order in the top 5 to 100 Å from which the SH arises, and was by and large dismissed as a small effect. However, the anisotropy is predicted by the form of the dipole-allowed SH generation from a surface layer and by the quadrupole-allowed form of the SH from the bulk of a centrosymmetric medium. In the case of Si(111) excited at 532 nm, the anisotropy in SH arising from the bulk is of the same order of magnitude as that arising from the Si-SiO<sub>2</sub> interface.<sup>5</sup> Most recently, the anisotropy of SH from the 2×1 and 7×7 reconstructed surfaces of Si(111) has been reported.<sup>8</sup>

Traditionally, SH from surfaces has been interpreted in terms of the nonresonant polarizability of nearly-free electrons.<sup>7</sup> This is largely because it presents a simple physical picture and also because it is more tractable theoretically. For silicon, the anisotropy in SH is perhaps not so surprising because much of the electronic response should be due to the electrons in the highly directional bonds between Si atoms. Furthermore, those bonds are arranged in a zincblende structure so that the total polarizability due to all bonds remains highly directional. In metals, on the other hand, we would expect electrons to be nearly free, and we would thus expect the nonlinear polarizability of the surface to be isotropic. However, if a suitable amount of the nonlinear polarizability were due to interband transitions, we might expect some SH anisotropy even from a metal. In this paper, we report the first observation<sup>9</sup> of just such anisotropy in the SH from a metal surface.

Studies were conducted on a Cu(111) surface. The 99.999% pure Cu crystal (monocrystals, OH) was oriented to 2° and mechanically polished with a series of grits ending with 1-μm diamond paste. The surface was optically similar to that of a commercial Cu mirror with a slight amount of "orange peel." The sample was atomically cleaned and or-

dered with cycles of 500-eV Ar ion sputtering and annealing at 500°C until Auger-electron spectroscopy indicated negligible C and O and a sharp 1×1 low-energy electron diffraction was observed. The background pressure in the UHV chamber was 4×10<sup>-11</sup> torr.

SH was generated in reflection from the Cu(111) surface using pulses of 1.06 μm radiation from a Nd-doped yttrium aluminum garnet laser. The pulses were 7 ns in duration, 7 mJ in energy focused to 5 mm<sup>2</sup> for a peak intensity of 20 MW/cm<sup>2</sup>, e.g., far below the damage threshold of Cu. The fundamental beam was passed through a polarizer and half-wave plate and then was incident on the sample 0.25° from the surface normal. SH at 532 nm so generated was then passed through filters, a half-wave plate, polarizer, monochromator, and finally detected with a photomultiplier tube and processed with gated electronics. Part of the input beam was split off and passed through a quartz plate to generate second harmonic against which the sample SH was normalized for laser fluctuations.

In Fig. 1, we show the sample SH intensity as we varied the input polarization angle where the SH intensity is that measured for the component of the SH field polarized perpendicular to the input polarization angle. (This was accomplished by simultaneously rotating both half-wave plates in

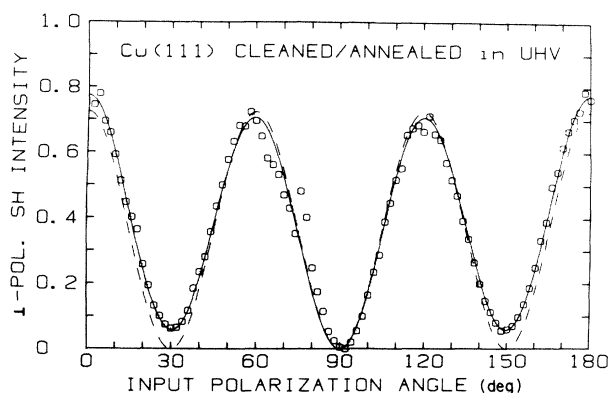


FIG. 1. Second-harmonic intensity from a Cu(111) surface as a function of the input polarization angle  $\phi$  where the SH field is measured with polarization perpendicular to the input polarization. Data taken with 0.25° angle of incidence (open circles). Theory assuming exactly normal incidence (dashed line). Theory accounting for nonzero angle of incidence (solid line).

the input and SH beam paths.) In the limit of exactly normal incidence, this would have been equivalent to measuring the vertically polarized SH generated from horizontally polarized input radiation and rotating the sample about its surface normal. In Fig. 1, we see three well-defined maxima and minima over  $180^\circ$  of angle rotation measured from the  $\hat{p}$ -polarized direction, thus immediately suggesting anisotropy compatible with the  $3m$  symmetry of the (111) surface. The orientation of the sample was in fact fixed with the surface  $(2\bar{1}\bar{1})$  axis along the  $\hat{s}$ -polarized direction: The structural mirror plane across the  $(2\bar{1}\bar{1})$  direction is evident in the symmetry in SH about  $90^\circ$  input ( $\hat{s}$ -) polarization angle.

To see if enough surface order would persist after the Cu(111) surface was exposed to air, we dosed the sample with  $O_2$  and watched the magnitude of the SH intensity maximum at  $60^\circ$  input polarization decrease to a saturation level 9% of the clean surface value after 2000 langmuirs (L, where  $1\text{ L} = 10^{-6}$  torr sec). After  $10^5$  L of additional  $O_2$  there was no change in SH. We then removed the sample from the vacuum chamber and placed it on a rotation stage on the optical table. In Fig. 2 we show the SH as a function of a sample rotation angle for  $\hat{s}$ -polarized SH generated with  $\hat{s}$ -polarized fundamental radiation incident on the sample at  $45^\circ$ . In Fig. 3 we show the SH again as a function of a sample rotation angle but this time with  $\hat{p}$ -polarized SH generated with  $\hat{p}$ -polarized fundamental. In both figures, the rotation angle is measured between the crystalline  $(2\bar{1}\bar{1})$  axis and the plane of incidence. The full  $3m$ -rotational symmetry (periodic every  $120^\circ$  and mirror through  $0^\circ$ ,  $120^\circ$ , and  $240^\circ$  points) is apparent.

The SH fields generated in reflection back into medium 1 from a nonlinear cubic medium 2 (both characterized by linear dielectric constants  $\epsilon_1$  and  $\epsilon_2$ , respectively) are derived from Maxwell's equations and suitable boundary conditions to be<sup>5,7</sup>

$$\begin{aligned} E_s &= \beta(k_0 P_{\text{eff},y}) , \\ E_p &= \alpha(k_x P_{\text{eff},z} + k_{2,z} P_{\text{eff},z}) , \end{aligned} \quad (1)$$

where the SH is induced by fundamental field  $\mathbf{E}(\omega)$  with incident wave vector  $\mathbf{k}(\omega) = (k_x(\omega), 0, k_z(\omega))$  defined in medium 2, the nonlinear source wave vector

$$\mathbf{k}_s = 2\mathbf{k}(\omega) = (k_x, 0, k_{z,z}), k_0 = 2\omega/c ,$$

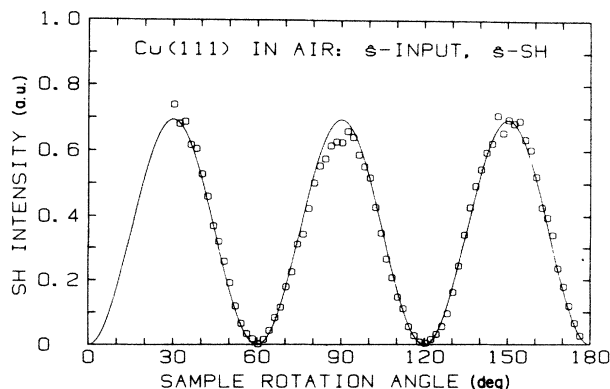


FIG. 2.  $\hat{s}$ -polarized second-harmonic intensity as a function of sample rotation angle for  $\hat{s}$ -polarized excitation. Data (open circles). Theory (solid line).

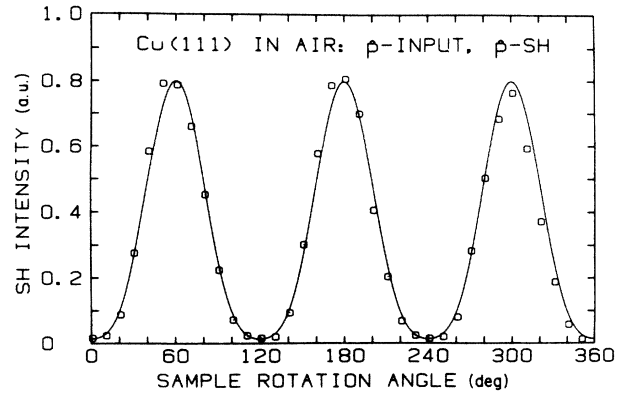


FIG. 3.  $\hat{p}$ -polarized second-harmonic intensity as a function of sample rotation angle for  $\hat{p}$ -polarized excitation. Data (open circles). Theory (solid line).

and the wave vectors for freely propagating SH in media 1 and 2 are  $\mathbf{k}_1 = [k_x, 0, (\epsilon_1 k_0^2 - k_x^2)^{1/2}]$  and  $\mathbf{k}_2 = [k_x, 0, (\epsilon_2 k_0^2 - k_x^2)^{1/2}]$ . In the above,

$$\alpha = 4\pi i \sqrt{\epsilon_1} k_0 / (\epsilon_2 k_{1,z} + \epsilon_1 k_{2,z})$$

and  $\beta = 4\pi i k_0 / (k_{1,z} + k_{2,z})$ . The effective nonlinear polarization is

$$\mathbf{P}_{\text{eff}} = \mathbf{P}_s(2\omega) + i\mathbf{P}_b(2\omega) / (k_{s,z} + k_{2,z}) , \quad (2)$$

where  $\mathbf{P}_s(2\omega)$  and  $\mathbf{P}_b(2\omega)$  are the surface and bulk nonlinear polarizations and Eq. (2) applies when  $\mathbf{P}_s(2\omega)$  is embedded in a layer with dielectric constant  $\epsilon_2$ . In bulk cubic media excited with a single incident beam, SH is dipole forbidden and  $\mathbf{P}_b$  has the form

$$P_{b,i}(2\omega) = \gamma \nabla_j [\mathbf{E}(\omega) \cdot \mathbf{E}(\omega)] + \zeta E_i(\omega) \nabla_j E_j(\omega) , \quad (3)$$

where  $\gamma$  and  $\zeta$  are frequency-dependent material parameters and the  $\hat{i}$  directions are along principal  $\langle 100 \rangle$  axes of the cubic crystal. The first term transforms as a vector and does not depend on the orientation of the principal axes: The second term leads to rotational anisotropy as it does depend on the orientation of the principal axes.

The surface layer of a (111) face of a cubic crystal such as copper has  $3m$  symmetry. The top atomic layer of the perfectly terminated surface is hexagonally close-packed and therefore  $6m$  symmetric, but if one includes the second or more atomic layers it is clear that the surface potential for the surface electrons should be  $3m$  symmetric. The surface nonlinear polarization  $\mathbf{P}_s$  has the dipole-allowed form

$$P_{s,i}(2\omega) = X_{ijk} E_j(\omega) E_k(\omega) , \quad (4)$$

where the  $\hat{i}$  directions are along the  $\hat{\xi} \parallel [2\bar{1}\bar{1}]$  and  $\hat{\eta} \parallel [01\bar{1}]$  crystalline axes in the plane of the surface and the surface normal,  $\hat{z}$  is parallel  $[111]$ . For the  $3m$ -symmetric surface there are only four independent nonzero elements of the susceptibility tensor  $\bar{X}$ :

$$X_{\perp\perp\perp}, X_{\perp\xi\xi} = X_{\perp\eta\eta} = X_{\perp\parallel\parallel}, X_{\xi\xi\xi} = X_{\eta\eta\eta} = X_{\parallel\parallel\parallel} ,$$

and

$$X_{\xi\xi\xi} = -X_{\eta\xi\eta} = -X_{\eta\eta\xi} = -X_{\xi\eta\eta} ,$$

the index  $\parallel$  denoting the general direction parallel to the surface. Only the last term  $X_{\xi\xi\xi}$  depends on the orientation

of the  $\hat{\xi}$  axis with respect to the excitation geometry and will lead to rotational anisotropy in the SH.

In general,  $E_i(2\omega)$  from both isotropic and anisotropic polarization terms from surface and bulk will have the form

$$A + Bf(\psi) \quad (5)$$

where  $A$  is a linear combination of the isotropic susceptibilities:  $X_{\perp\perp\perp} - \gamma$ ,  $X_{\perp\parallel\parallel} - \gamma$ ,  $X_{\parallel\perp\parallel}$ , and  $\zeta$ ,  $B$  is proportional to the anisotropic susceptibilities  $X_{\xi\xi\xi}$  and  $\zeta$ , and  $f(\psi)$  is a linear combination of  $\cos(3\psi)$  and  $\sin(3\psi)$ . All the coefficients are fixed by the dielectric constants and excitation geometry.

Using  $\hat{s}$ -polarized fundamental and looking only at the  $\hat{s}$ -polarized SH, one then sees that none of the isotropic susceptibilities will contribute since  $E_{\parallel}$  is zero and therefore one expects  $A=0$ . For this excitation geometry,  $f(\psi) = \sin(3\psi)$  and the fit of  $|E_s|^2 = |B \sin(3\psi)|^2$  (solid line) with the data (open circles) in Fig. 2 is extremely good. Looking at  $\hat{p}$ -polarized input and  $\hat{p}$ -polarized SH we have no such cancellation of  $A$ . The data in Fig. 3 then fit Eq. (5) with  $A/B = -1.3$  and  $f(\psi) = \cos(3\psi)$ , again with good agreement.

In the limit of normal incidence, input and SH fields must be polarized parallel to the surface plane, and as for the case of  $\hat{s}$ -input field and  $\hat{s}$ -SH field we expect  $A$  is zero. For vertically polarized input and horizontally polarized SH, one expects  $E(2\omega) = B \cos(3\psi)$  as the sample is rotated angle  $\psi$  about its normal. In Fig. 1 the data in circles are fitted relatively well by the dashed curve of  $|B \cos(3\psi)|^2$ . In our experiment, however, we used  $0.25^\circ$  angle of incidence. For  $\psi$  fixed at  $90^\circ$ , the correct form for  $E$  perpendicular to the input polarization angle  $\phi$  (measured from the  $\hat{p}$ -polarization direction) is given by

$$E_{\phi} = B \cos(3\phi) + C \cos\phi \sin^2\phi + D \cos^2\phi \sin\phi + E \sin(3\phi) \quad (6)$$

The fit to this function is plotted with a solid line in Fig. 1 and the fit to the data is again extremely good using  $C/B = 1.27 \exp(i70.7^\circ)$  and  $D/B = E/B = 0$ .

We see then that SH from Cu(111) clean or with surface oxide has a measurable SH rotational anisotropy. This must be due to interband transitions since one would expect surface and bulk susceptibilities  $X_{\xi\xi\xi}$  and  $\zeta$  to be zero for a purely free-electron response. The linear optical response for copper would suggest that while at  $1.06 \mu\text{m}$ , the response is due largely to free electrons in a Drude-like metallic way [ $\epsilon(\omega) = -51.3 + i5.16$ ], at  $0.532 \mu\text{m}$  (the SH wavelength), the electronic response contains contributions from interband transitions involving  $d$ -band electrons [e.g., responsible for the apparent red color of Cu and the value of  $\epsilon(2\omega) = -5.63 + i5.39$ ].

By calibrating the SH signals against a quartz plate excited at a Maker fringe, we find that  $|X_{\xi\xi\xi} - a\zeta|/d_{111} = 1.4 \times 10^{-3}$  for the clean surface in vacuum and  $= 4.3 \times 10^{-4}$  for the surface in air. The coefficient  $a$  is  $8.58 \times 10^{-2} \exp(i5.3^\circ)$ .  $d_{111}$  is the quartz nonlinear coefficient  $= 1.1 \times 10^{-9}$  esu. Note that  $|X_{\xi\xi\xi} - a\zeta|$  has this extremely large value because we have defined  $X_{\xi\xi\xi}$  so that it is embedded in a layer with the dielectric constant of bulk copper. The value would be much smaller had we chosen the dielectric constant of the layer to be that of vacuum. At present we do not know the

phases of the susceptibilities and cannot determine the value of  $\zeta$  or  $X_{\xi\xi\xi}$  alone. We do know, however, that the change in SH upon oxidizing the sample is due to a change in  $X_{\xi\xi\xi}$ . We cannot assume  $X_{\xi\xi\xi}$  of the oxidized Cu surface is small because bulk  $\text{Cu}_2\text{O}$  has an interband transition near  $2\omega$ . We can assume that the SH bulk signal comes from the top 100 Å of the surface since this is the depth at which SH is generated by attenuated fields and attenuated in radiation so that it is reduced by  $e^{-2}$  with respect to the SH generated at the surface.

We now consider some of the implications of finding this strong rotational anisotropy in metals. First we must reconsider some of the earlier SH studies of metals<sup>3,7</sup> and semiconductors<sup>2,6,10</sup> that neglected anisotropy and the importance of interband transitions. SH studies on crystalline metals and semiconductors should be checked to be sure interpretations are based on measurements of changes to the individual elements of  $\bar{X}$  which are material-dependent parameters, rather than to some superposition of those elements which is dependent on the excitation geometry. For example, simply repeating an SH experiment on the reverse side of a (111) sample is the same as rotating the sample axes  $180^\circ$ , e.g., changing  $E(2\omega) = A + B$  to  $A - B$ . Since  $A$  may contain the response of both free electrons and interband transitions, while  $B$  contains only the response due to interband transitions,  $A$  and  $B$  should in general behave differently upon atomic or molecular adsorption and will surely behave differently if surface order is changed. Thus, the SH may be different not only in magnitude but also behavior on two sides of a crystal.

Secondly, we may exploit the fact that the anisotropic term is a probe of interband transitions free of free electron, Drude-like, susceptibility. In particular, we might expect that adsorbate-induced changes in  $X_{\xi\xi\xi}$  could mean participation of  $d$ - or  $p$ -like electronic states of the metal in binding the adsorbate. Since this participation is likely to be different for adsorbates on different binding sites, one expects that different binding sites will be more easily distinguished [compare to study of CO on top and bridge sites on Rh(111) in Ref. 2] by following  $X_{\xi\xi\xi}$  and at least one of the isotropic susceptibilities. By correlating the isotropic susceptibilities with  $X_{\xi\xi\xi}$  one might, in turn, be able to remove the interband contribution to the isotropic susceptibilities and deduce changes in the Fermi level and/or the free-electron density of the surface.

Through the polarization properties of  $X_{\xi\xi\xi}$  and susceptibility elements with projections perpendicular to the surface, one may be able to get polarization information about interband transitions on the surface. While electronic EELS might be able to do this more easily, SH would have the advantage of time-resolution during adsorption or desorption processes and also may be done on surfaces in high-pressure (atmospheric) environments.

Finally, and perhaps the most useful property of this rotational anisotropy is that  $X_{\xi\xi\xi}$  is a measure of the surface order and may thus be used to monitor the order as it is changed. The time evolution of laser-induced melting of the Si(111) surface was studied using the rotational anisotropy of SH generated by a time-delayed probe pulse.<sup>6</sup> A similar experiment on Cu(111) is currently in progress.

In conclusion, we show for the first time that crystalline metals exhibit strong SH rotational anisotropy. The form of this anisotropy is fully predicted by the theory of dipole-

allowed SH from the surface and quadrupole-allowed SH from the centrosymmetric bulk. Future SH studies of metallic substrates should take into account this anisotropy in analyzing SH response to adsorbates. The anisotropic susceptibility of the surface and bulk can only arise from inter-

band transitions: They are independent of free-electron contributions. This new sensitivity to interband transitions may allow SH to be more sensitive to adsorbate interactions with different electronic states, e.g., binding sites. SH may also be used to monitor atomic ordering on metal surfaces.

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<sup>9</sup>Weak anisotropy in the SH from Rh(111) was observed but not published by the authors of Ref. 5.

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