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Second harmonic generation from the Cu(001) surface

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Abstract

We report on measurements of the second harmonic (SH) yield from a Cu(001) surface in the wavelength range between 740 nm and 840 nm which is below the one photon excitation threshold of d-electrons. The SH-yield varies strongly with the azimuthal angle of the Cu crystal indicating a significant contribution of bulk anisotropic SH generation.

Keywords: Copper; Low index single crystal surfaces; Metallic surfaces; Second harmonic generation

1. Introduction

Optical second harmonic generation (SHG) at surfaces of simple and noble metals has attracted considerable interest in the past, both from the theoretical [1–5] as well as from the experimental side [6–8]. Partly this interest comes from the fact that in centrosymmetric media like the fcc and bcc crystals SHG due to nonlinear dipole polarization is forbidden by symmetry as long as the electric dipole approximation is valid. At the surface (or at buried interfaces) the inversion symmetry is broken and therefore SHG is possible. In many cases the effective depth in which SH is generated is restricted to the range where the electron density is changed with respect to the bulk. This is typically of the order of a single atomic layer although it can reach several 10 Å in special cases [9]. Because of the much larger skin depth of light of the order of 100 Å buried interfaces can also be accessed in this way. However, going beyond the electric dipole approximation one recognizes that there are also bulk sources of SHG [2]. These are induced by the strong spatial variation of the electric (and magnetic) fields of the light inside the nonlinear medium causing nonlinear dipole contributions from the spatial variation of the induced nonlinear quadrupole and magnetic dipole moments. This effect is especially strong in metals due to the strong absorption and high refractive indices and therefore, the resulting bulk SH amplitude can be comparable in size to that of the surface.

In general it is not possible to separate these two contributions completely within a single experiment, i.e., without investigating different surfaces or modifying the surface by adsorbates etc. However, for the (001) surfaces of cubic crystals the surface response is isotropic with respect to the azimuthal orientation of the crystal surface and therefore a possible anisotropy is caused solely by the bulk. Such contributions have been observed for the Al(001) surface [11,12], but have been found to be small for the (001) noble metal/air interfaces [11].

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In this publication we show, that for the clean Cu(001) surface prepared under ultra high vacuum (UHV) conditions these anisotropic bulk contributions are of the same order of magnitude as the isotropic effective surface contribution at a photon energy of the incident light, ~ 1.5 eV which is much below the threshold for one photon interband excitation in Cu(001) of about 2 eV [5].

2. Theory

The total nonlinear polarization at 2ω induced in a medium with cubic symmetry is given by [13]:

$$\begin{aligned} P_i(2\omega) = & \sum_{jk} \chi^{S}_{ijk} E_j(\omega) E_k(\omega) \\ & + (\delta - \beta - 2\gamma)(\boldsymbol{E} \cdot \nabla) E_i + \beta E_i (\nabla \cdot \boldsymbol{E}) \\ & + \gamma \nabla_i (\boldsymbol{E} \cdot \boldsymbol{E}) + \xi E_i \nabla_i E_i + \ldots \end{aligned} \qquad (1)$$

with β, γ, δ, and ξ the phenomenological constants introduced by Bloembergen [14]. The term in the first line describes the surface response. For a (001) surface of a cubic crystal there are actually only three independent elements of the surface susceptibility χ^S: $\chi^S_{xzx} = \chi^S_{yzy}$, $\chi^S_{zxx} = \chi^S_{zyy}$, and χ^S_{zzz}. If there is only a single fundamental wave involved then both terms in the second line of Eq. (1) vanish. The first term in the third line gives the isotropic bulk contribution. It has been shown by several authors that this term can be combined with χ^S in an effective surface term χ. Note, however, that this isotropic bulk contribution affects only the p-polarized SH light while the isotropic s-polarized part comes entirely from the surface.

Using the notation introduced by Sipe et al. [13] the $\boldsymbol{E}$-field amplitudes of the p- and s-polarized SH-light generated from the isotropic part of the nonlinear polarization are given by:

$$\begin{aligned} E^{\mathrm{surf}}_{\mathrm{p}}(2\omega) &= 2\mathrm{i}\frac{\omega}{c} E_0^2 \left(a^{\mathrm{surf}}_{\mathrm{p}} \cos^2\varphi + b^{\mathrm{surf}}_{\mathrm{p}} \sin^2\varphi \right), \\ E^{\mathrm{surf}}_{\mathrm{s}}(2\omega) &= 2\mathrm{i}\frac{\omega}{c} E_0^2 \left(a^{\mathrm{surf}}_{\mathrm{s}} \cos\varphi \sin\varphi \right), \end{aligned} \qquad (2)$$

with

$$\begin{aligned} a^{\mathrm{surf}}_{\mathrm{p}} = & A_{\mathrm{p}} [F_c \chi_x 2 f_{\mathrm{c}} f_{\mathrm{s}} \\ & + N^2 F_{\mathrm{s}} (\chi_{zxx} f_{\mathrm{c}}^2 + \chi_{zzz} f_{\mathrm{s}}^2)] t_{\mathrm{p}}^2 \end{aligned}$$

$$b^{\mathrm{surf}}_{\mathrm{p}} = A_{\mathrm{p}} N^2 F_x \chi_{zxx} t_{\mathrm{s}}^2,$$

$$a^{\mathrm{surf}}_{\mathrm{s}} = A_s \chi_{xzx} 2 f_{\mathrm{s}} t_{\mathrm{p}} t_{\mathrm{s}},$$

and φ the angle of the $\boldsymbol{E}(\omega)$ vector of the incident light with respect to the optical plane. p,s denote the components of $\boldsymbol{E}(2\omega)$ parallel and perpendicular to this plane. The anisotropic bulk contributions for the ⟨100⟩ and ⟨110⟩ azimuth are given by:

$$\begin{aligned} E^{\mathrm{bulk}}_{\mathrm{p,s}}(2\omega) = & 2\mathrm{i}\frac{\omega}{c} E_0^2 A_{\mathrm{p,s}} \frac{n\xi}{8(n f_{\mathrm{c}} + N F_{\mathrm{c}})} \\ & \times \left(a^{\mathrm{bulk}}_{\mathrm{p,s}} \pm c^{bulk}_{\mathrm{p,s}} \right), \end{aligned} \qquad (3)$$

with

$$\begin{aligned} a^{\mathrm{bulk}}_{\mathrm{p}} = & f_{\mathrm{s}} [F_{\mathrm{c}} t_{\mathrm{s}}^2 \sin^2\varphi \\ & + \left(3 F_{\mathrm{c}} f_{\mathrm{c}}^2 + 4 F_{\mathrm{s}} f_{\mathrm{s}} f_{\mathrm{c}} \right) t_{\mathrm{p}}^2 \cos^2\varphi, \end{aligned}$$

$$c^{\mathrm{bulk}}_{\mathrm{p}} = f_{\mathrm{s}} F_{\mathrm{c}} \left(f_{\mathrm{c}}^2 t_{\mathrm{p}}^2 \cos^2\varphi - t_{\mathrm{s}}^2 \sin^2\varphi \right),$$

$$a^{\mathrm{bulk}}_{\mathrm{s}} = -2 f_{\mathrm{s}} f_{\mathrm{c}} t_{\mathrm{s}} t_{\mathrm{p}} \cos\varphi \sin\varphi,$$

$$c^{\mathrm{bulk}}_{\mathrm{s}} = -a^{\mathrm{bulk}}_{\mathrm{s}},$$

with the + sign in Eq. (3) for the ⟨100⟩ and the − sign for the ⟨100⟩ azimuth. The f_{s}, f_{c}, F_{s}, F_{c}, t_{s}, t_{p}, A_{s}, and A_{p} are defined as in Ref. [13], n and N are the refractive indices at ω and 2ω, respectively.

3. Experiment

A similar experimental setup as in Ref. [10] was used. A Cu sample with a miscut less than 0.2° was cleaned in ultrahigh vacuum (base pressure 4×10^{-11} mbar) by 1 keV Ar^+ sputtering and subsequent annealing to 900 K. All contaminations were below 1 at. % as checked by Auger electron spectroscopy. The sample was mounted onto a manipulator which allowed the azimuthal rotation of the crystal by 60° with a wobble estimated less than 1°.

The light of a femto-second pulsed Ti-sapphire laser was focused down to ~ 50 μm diameter onto the sample through a fused silica window of the UHV chamber. Using a Babinet–Soleil compensator as $\lambda/2$ wave plate the polarization axis of the linear polarized light of the laser could be rotated. The frequency doubled light generated at the surface of the Cu crystal left the UHV chamber through a second window together with the fundamental light reflected from the Cu surface. While the latter was blocked by two Schott BG36 colored glass filters of 2 and 3 mm thickness, the SH-light was detected by a photomultiplier (Hamamatsu R268) and measured using lock-in technique by chopping the incident light beam. Possibly generated SH-light in the incident beam was blocked by a OG570 colored glass filter in the incident beam path. The polarization of the outgoing SH-light was measured by placing a Glan–Thompson calcite polarizer after the first BG36 filter in the beam path.

4. Results

In Fig. 1 the total SH-intensity is plotted versus the polarization angle φ of the incident light at a wavelength of 840 nm for different azimuthal angles ψ of the Cu(001) surface. The polar angle relative to the surface normal was about 38°. $\varphi = 0°$ corresponds to p-polarized incident light, $\psi = 0°$ corresponds to the ⟨110⟩ direction. Clearly, very large changes in shape of these curves for different azimuthal angles are observed which cannot be attributed to possible changes in the polar angle of about 1° during rotation of the azimuthal angle. Note also the (nearly) symmetric shape of the measured SH-curve for the ⟨110⟩ and the ⟨100⟩ azimuth with respect to the input polarization angle φ around 0° (p-polarized incident light) and 90° (s-polarization) in agreement with the symmetry analysis in section 2: For p-polarized outgoing SH E-field amplitude only terms with $\sin^2 \varphi$ and $\cos^2 \varphi$ occur in Eqs. (2) and (3) while for s-polarization the φ dependence is described by $\sin \varphi \ \cos \varphi$ for all terms. For the incident light polarization along other azimuths than the two high symmetry directions additional terms come into play (not included in Eqs. (2) and (3)) producing the asymmetry shown in Fig. 1 for the

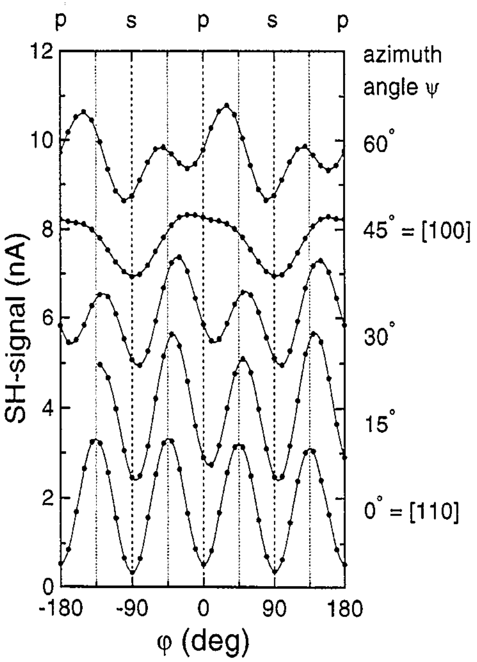

Fig. 1. Total SH intensity as a function of the angle φ of the polarization direction of the incident fundamental light at the wavelength $\lambda = 840$ mm for various azimuth angles ψ. $\varphi = 0$ corresponds to p-polarization. The curves are offset by 2 nA with respect to each other.

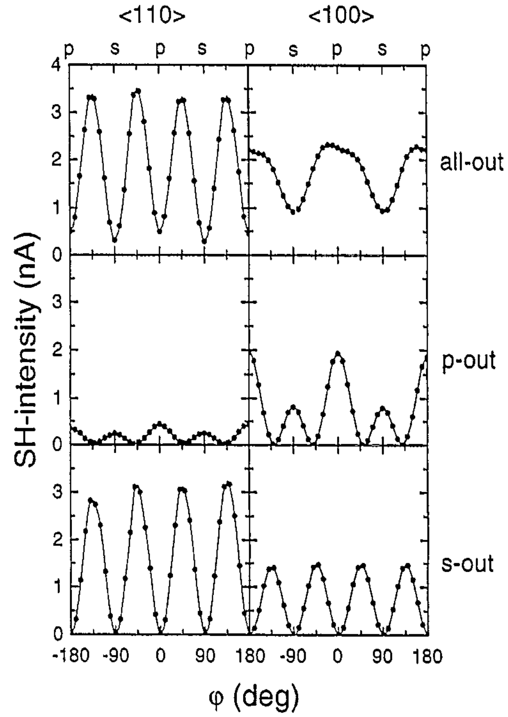

Fig. 2. SH intensity as a function of the polarization of the incident light at wavelength $\lambda = 840$ nm for the ⟨110⟩ (left side) and the ⟨100⟩ (right side). Top panels: total SH intensity, middle panels p-polarized part, and bottom panels s-polarized part of the SH intensity.

15°, 30°, and 60° azimuth angle. For the following analysis we restrict the discussion to the ⟨110⟩ and ⟨100⟩ azimuthal directions. Fig. 2 shows the SH intensity as a function of the input polarization for these two high symmetry azimuthal directions, in the two top panels again the total SH signal and in the panels below its p- and s-polarized part. The intensities are uncorrected for the additional losses due to the analyser in the outgoing beam path. For the ⟨110⟩ azimuth the SH intensity varies strongly with the input polarization. An especially strong signal is observed for the mixed (m), $\varphi = 45°$, input polarization. This signal is found to be purely s-polarized. As can be seen from Eq. (2) its part independent of the azimuthal angle, i.e., the isotropic contribution, is generated entirely at the surface from a single matrix element χ_{xzx}. It was already mentioned above that there is no isotropic bulk contribution to the s-polarized SH light. Comparing this s-polarized component with that of the ⟨100⟩ azimuth orientation (see the two bottom panels of Fig. 2) one finds a dramatic difference in the SH amplitude by a factor of 2 at 790 nm which is due to the bulk anisotropic component. This difference even increases for shorter wavelength. From Eqs. (2) and (3) we find the intensities:

$$I^{\langle 100\rangle}_{\mathrm{m}\rightarrow\mathrm{s}}(2\omega) \propto |\chi_{xzx}|^2, \tag{4}$$

$$I^{\langle 110\rangle}_{\mathrm{m}\rightarrow\mathrm{s}}(2\omega) \propto |\chi_{xzx} - 2\xi'|^2, \tag{5}$$

with $\xi' = nf_\mathrm{c}\,\xi/(8(nf_\mathrm{c} + NF_\mathrm{c}))$. Without knowing the phase between χ_{xzx} and ξ' we can estimate only [15]:

$$0.4 < |2\xi'|/|\chi_{xzx}| < 2.4 \tag{6}$$

A similar relation can be obtained from the p-polarized components of the SH light. Here the ratio $I^{\langle 110\rangle}(2\omega)/I^{\langle 110\rangle}(2\omega)$ for the p → p and the s → p polarization component is even larger, 3.5 and 4.5, respectively. However, because in this case also isotropic bulk terms contribute, a relation to pure surface terms cannot be derived.

We also investigated the influence of oxygen on the SH intensities and found that even an exposure of 400 Langmuir (L) O_2 does not remove the observed anisotropy in the SH light although it drastically increases the SH yield for p-polarized incident light.

5. Discussion and conclusions

Our results on the clean Cu(001) surface differs remarkably from the results obtained by Koos, Shannon, and Richmond on the Cu(001)/air interface who found only a very small azimuthal anisotropy of the SH yield. One might attribute this to the existence of an oxide layer and other adsorbed molecules on the surface which generate SH by themselves and indeed for p-polarized incident light a dramatically increased SH intensity is observed for the oxidized surface. However, this point of view can be excluded because even a surface exposed to 400 L O_2 exhibits a strong, although different, azimuthal SH anisotropy. Considering the different photon energies used in the two experiments, 1.45–1.65 eV (840–740 nm) in our case and 1.16 eV (1060 nm) in their case one finds that the latter is just at the threshold for two photon interband transitions between d and s bands which occur along the Δ direction in the Brillouin zone. For the higher energy used in our experiments additional interband transitions along the Σ direction become energetically possible. Therefore, the reduced contribution of two photon interband transitions might be responsible for the smaller azimuthal SH anisotropy in the experiment at the larger wavelength. But note, that in both cases the photon energy is well below the one photon interband transition threshold.

For the Al(111) surface the influence of steps has been discussed widely [16]. It was shown that steps may contribute significantly to the anisotropic SH response. Especially for vicinal surfaces an increase of the SH intensity by more than an order of magnitude was observed. However, for Cu(001) we can rule out a significant contribution to the observed anisotropy for the following reasons: Even in the presence of steps the 4-fold symmetry of the (001) surface is conserved excluding any anisotropy from the surface SH response. The only possible reason for a surface anisotropy could be the small, 0.2°, miscut of the (001) surface. Despite the large enhancement factor observed for steps this cannot contribute significantly because the average (001) terrace width are shown to exceed several 100 nm [17]. In addition, a two fold instead of the 4 fold anisotropy would be expected.

In a recent paper Hübner, Bennemann, and Böhmer [5] pointed out the possibility of extracting information about the electronic structure from the surface SH response of a metal surface. One of their results was that for noble metals the $I_{s\rightarrow p}(2\omega)$ response should be much smaller than the $I_{p\rightarrow p}(2\omega)$ response when the one photon energy is below the d-band excitation threshold and should increase for larger energies. Although their theory agrees well with recent experimental data of Böhmer [18] on the Cu(001)/air interface, it completely disagrees with our present results. Here, the $I_{s\rightarrow p}(2\omega)$ and $I_{p\rightarrow p}(2\omega)$ signals are comparable at $\lambda = 790$ nm which is far below the one photon interband excitation threshold. This discrepancy, however, is not unexpected in view of the large anisotropy observed in our experiments. Their model does not include any anisotropy and is restricted to the surface nonlinear response. If we accept their result for the surface contribution, we can conclude that not only the anisotropic part of the bulk SH contribution is large but also its isotropic part: Along the $\langle 100\rangle$ azimuth the anisotropic contribution for the $s\rightarrow p$ polarization combination is zero, but still a large SH intensity is observed.

In conclusion we have shown, that the Cu(001) surface exhibits a strong azimuthal anisotropy in the SH yield due to the anisotropic bulk response. This strong anisotropy indicates that already at photon energies of about 1.5 eV interband transitions are important contributions to the SH yield.

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