

AD-A265 205



DOCUMENTATION PAGE

OMB No. 0704-0188

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2. REPORT DATE 27 May 1993		3. REPORT TYPE AND DATES COVERED Technical 5/92-5/93	
4. TITLE AND SUBTITLE Surface Second Harmonic Generation Studies of Stepped Ag(111) Electrode Surfaces		5. FUNDING NUMBERS ONR N00014089-J-1261	
6. AUTHOR(S) K. A. Friedrich and G. L. Richmond			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Oregon Eugene, OR 97403		8. PERFORMING ORGANIZATION REPORT NUMBER ONR Technical Report # 3	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Program 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES DTIC ELECTE JUN 03 1993 S B D			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release: distribution unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The rotational anisotropy in the optical second harmonic response from flat and stepped Ag electrode surfaces biased in an electrolyte solution have been examined. Compared to the flat Ag(111) surface, the stepped surfaces show a pronounced effect due to the lowering of the surface symmetry. The results are interpreted in terms of a pseudo mirror plane at these steps. 93 6 02 071 93-12466			
14. SUBJECT TERMS Stepped crystal electrode surfaces; optical second harmonic generation		15. NUMBER OF PAGES 18	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT

OFFICE OF NAVAL RESEARCH

Grant N00014-89-J-1261

R&T Code 4131038

Technical Report No. 3

"Surface Second Harmonic Studies of Stepped Ag(111) Electrode Surfaces"

by

K.A. Friedrich and G.L. Richmond

Submitted to *Chem. Phys. Lett.*

Department of Chemistry
University of Oregon
Eugene, OR 97403

May 1993

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Surface Second Harmonic Generation Studies of Stepped Ag(111) Electrode Surfaces

K.A. Friedrich and G.L. Richmond
Chemical Physics Institute
University of Oregon, Eugene, OR 97403

Abstract:

The rotational anisotropy in the optical second harmonic response from flat and stepped Ag electrode surfaces biased in an electrolyte solution have been examined. Compared to the flat Ag(111) surface, the stepped surfaces show a pronounced effect due to the lowering of the surface symmetry. The results are interpreted in terms of a pseudo mirror plane at these steps.

I. Introduction

One aspect of the growing field of surface second harmonic generation (SHG) which has attracted much attention recently is the sensitivity of the technique to surface symmetry.¹⁻⁵ As the surface of a single crystal is rotated azimuthally, the angular variation in the SH intensity which results, referred to as rotational anisotropy, can be correlated with the symmetry of the surface atomic structure.^{6, 7} Optical phase information associated with this type of data taken over a series of incident wavelengths can also provide information about surface electronic structure.⁸ Such types of experiments are ideal for measuring surface properties in-situ where the commonly used ultra-high vacuum (UHV) techniques are inapplicable.^{9, 10}

In this paper the first study of vicinal metal electrode surfaces examined by surface SHG is reported. The results have important consequences for SH studies of electrode surface reconstruction^{11, 12} and for future studies in which one attempts to understand the important and sometimes dominating role of steps and defects in surface chemistry. A pronounced effect in the

Current Address: Institut für Energieverfahrenstechnik, Forschungszentrum Jülich GmbH, Postfach 1913, D-5170 Jülich, Germany

SH response is seen when steps are present and reflect the lowering of symmetry from C_{3v} (the symmetry of the terraces) to C_s . The response from these vicinal surfaces can be well described using existing models. There is no evidence that steps or defects are the sole source of the anisotropy for the flat Ag(111) surface as has been suggested by Janz et al. for Al surfaces.^{13, 14}

The studies involve rotational anisotropy measurements on a flat Ag(111) surface, a Ag(211) surface which has a high density of steps and a vicinal (111) surface. All are studied in 0.10 M NaClO₄ at selected applied potentials to either minimize or maximize the effect of the dc electric field across the interface. Previous comparative measurements of Ag(111) in an electrochemical environment and in UHV have shown that when the Ag(111) surface is biased at the potential of zero charge (PZC), the SH response in solution under both resonant and nonresonant conditions is nearly identical in magnitude and phase angle with the response in UHV.¹⁵ In these solution studies the applied dc field is used to elucidate the role of the steps in the SH response. The studies are performed under nonresonant conditions¹⁶ to avoid alterations of the electronic structure which can result from the increased step density.

II. Experimental

The crystals used for this study were 99.999% pure Ag (Monocrystals, Cleveland, OH). These consisted of one (111) oriented crystal, one (211) oriented crystal ($19^\circ 28'$ from the (111) surface) and two vicinal Ag(111) crystals which were cut with an offset angle of 4° towards the $[2\bar{1}1]$ direction. All were oriented within 1° as verified by Laue X-ray diffraction. For the solution experiments, the mechanically polished surface (1mm) was maintained under an inert O₂ free atmosphere throughout the electrochemical polishing and subsequent transfer into the electrochemical cell. All solutions were prepared from high purity salts and Nanopure water, and the electrolyte was continuously purged with O₂ free N₂ during the electrochemical experiments to avoid oxide formation. The electrochemical cell design has been described previously.¹⁷ All potentials for the electrochemical measurements are measured against the Saturated Calomel reference electrode potential (SCE).

The optical measurements were performed with 1064 nm excitation from the fundamental output from a 10 Hz Nd:YAG laser producing 10ns pulses. The effective angle of incidence for the solution experiments described here is 30°. The incident fluence of the pulses was always set to 17 mJ/cm², stable within 5%. High quality Glan-Taylor polarizers were used for controlling the polarization of the incident and generated SH light. The SH light passing the monochromator was detected by a photomultiplier tube using a fast preamplifier with gated electronics.

III. Theoretical Considerations

The second order polarization that gives rise to surface sensitive second harmonic generation is normally described by a series of multipole terms up to the first derivatives:^{18, 19}

$$I_{s,s}^{(2\omega)}(2\omega) = \tilde{\chi}^D : E(\omega)E(\omega) + \tilde{\chi}^P : E(\omega)\nabla E(\omega) - \nabla \left[\tilde{\chi}^Q : E(\omega)E(\omega) \right] + \frac{c}{i2\omega} \nabla \times \left[\tilde{\chi}^M : E(\omega)E(\omega) \right] \quad \text{Eq. 1}$$

The first 2 terms are electric dipole in nature, the third and fourth describe the electric quadrupole contribution and magnetic dipole contribution respectively. The first term, the dipole allowed surface term, is the most important for this study where only the in-plane second order polarization is measured. Terms involving a gradient can be neglected since the tangential components of the incident electric field are continuous across the interface. To probe the in-plane response from these surfaces, incident light polarized either parallel (p) or perpendicular (s) to the plane of incidence is used and only the s-polarized SH radiation is detected.

SHG derives its surface sensitivity from the dipole allowed surface term. Higher order bulk terms (quadrupole in nature) are inseparable from the dipole term, but have been shown to be small in metals compared to the surface terms²⁰ and are therefore neglected. The surface allowed dipole contribution can be written as:

$$P_{eff}^{(2)}(2\omega) = \tilde{\chi}^D : E(\omega)E(\omega) \quad \text{Eq. 2}$$

where $\chi^{(2)}$ is the second order susceptibility tensor reflecting the optical properties of the surface layer. If the SH intensity is recorded as a function of azimuthal angle the variation in intensity reflects the overall symmetry of the surface. A crystalline surface of C_{3v} symmetry, e.g. a (111) face, yields the following angle dependence for s-polarized SH radiation if excited by a s-polarized pump beam at frequency ω .

$$I_{s,s}^{(2\omega)}(\varphi) \propto |d_{11}^{(3)} \sin(3\varphi)|^2 \quad \text{Eq. 3}$$

with $d_{11}^{(3)} = F_s \chi_{xxx} f_s f_s$

$$I_{p,s}^{(2\omega)}(\varphi) \propto |d_{11}^{(3)} \sin(3\varphi)|^2 \quad \text{Eq. 4}$$

with $d_{11}^{(3)} = F_s \chi_{xxx} f_k f_k$

where the subscripts s/p refer to the polarizations of the fundamental and SH light, respectively. The factors $F_{s,k}$ and $f_{s,k}$ represent the complex Fresnel numbers of the fundamental and SH light for reflection under the respective polarization condition.

Steps on a crystal surface are sites of low coordination due to the broken bonds which exist there. Locally, at the step sites the symmetry of the terraces is reduced to C_s , since only the mirror plane normal to the steps is preserved. If the crystal is cut such that all of the steps are oriented in one direction the overall surface symmetry is also reduced to C_s . From a tensor analysis of C_s symmetry²¹ additional one and two fold rotational amplitudes can be expected along with the threefold amplitude of a flat (111) surface. For the polarization combinations used here the SH intensity for C_s symmetry can be written as:

$$I_{s,s}^{(2\omega)}(\varphi) \propto |d_{11}^{(1)} \sin(\varphi) - d_{11}^{(3)} \sin(3\varphi)|^2 \quad \text{Eq. 5}$$

with $d_{11}^{(1)} = \frac{1}{4} F_s (3\chi_{xxx} + \chi_{xyy} + \chi_{yyx}) f_s f_s$

and $d_{11}^{(3)} = \frac{1}{4} F_s (\chi_{xxx} - (\chi_{xyy} + 2\chi_{yyx})) f_s f_s$

and

$$\begin{aligned}
I_{p,s}^{(2\omega)}(\varphi) &\propto \left| d_{12}^{(1)} + d_{13}^{(1)} \sin(\varphi) - d_{14}^{(2)} \sin(2\varphi) + d_{11}^{(3)} \sin(3\varphi) \right|^2 \\
\text{with } d_{12}^{(1)} &= \frac{1}{4} F_s (\chi_{xxx} + 3\chi_{xyy} - 2\chi_{yyx}) f_k f_k, \quad d_{13}^{(1)} = F_s \chi_{xxz} f_k f_k, \\
d_{14}^{(2)} &= \frac{1}{2} F_s (\chi_{xxx} - \chi_{yyx}) f_k f_k \\
\text{and } d_{11}^{(3)} &= \frac{1}{4} F_s (\chi_{xxx} - (\chi_{xyy} + 2\chi_{yyx})) f_k f_k
\end{aligned}
\tag{Eq. 6}$$

For the stepped surfaces studied which were cut with an offset angle in the $[2\bar{1}\bar{1}]$ direction from the (111) surface, the coordinate system was chosen so that the azimuthal angle φ is defined as the angle between the direction perpendicular to the steps (which is the $[2\bar{1}\bar{1}]$ direction for the vicinal surface, and the $[1\bar{1}\bar{1}]$ direction for the (211) surface) and the projection of the incident wave vector parallel to the surface (see Fig. 1). The x direction in the above equations is therefore equivalent for the different surfaces and in the direction perpendicular to the steps. As can be seen from Equation 3 for s/s polarization conditions the intensity at an azimuthal angle of 30° is directly proportional to $|\chi_{xxx}|^2$, the polarization in the direction perpendicular to the steps.

IV. Results and Discussion

Figure 2 shows the rotational anisotropies obtained under s/s polarization conditions from the three surfaces in 0.1 M NaClO₄ electrolyte with an applied potential of -0.5 V vs SCE. This potential is near the PZC for all of these surfaces. Fig 2(a) shows the rotational anisotropy from Ag(111) which is similar to previous work.^{22, 23} The data reflects the C_{3v} symmetry of this surface and is in excellent agreement with Equations 3. Fig. 2(b) shows the rotational anisotropy of a surface vicinal to the Ag(111) ($\theta=4^\circ$), which in the case of only monoatomic steps, corresponds to a notation introduced by Lang et al.²⁴ of $14(111)\times(100)$. In Fig. 2(c) the rotational anisotropy of the SH signal of a crystal with a nominal (211) orientation is shown. This is highly stepped surface with a Lang notation of $3(111)\times(100)$. The data from the stepped surfaces in Fig. 2(b) and 2(c) clearly deviate from the pattern expected for a C_{3v} symmetry and can be explained by an additional onefold contribution to the SHG superimposed onto the threefold

contribution of the terraces. The only mirror plane preserved for the stepped surfaces is at $\phi=0^\circ$. The existence of this mirror plane is evident in all rotational anisotropies of Fig. 2, since the intensity at 0° and 90° is zero. Similar to the SH pattern from semiconductor surfaces^{25, 26} the signal from stepped metal surfaces exhibits a strong influence of the steps.

To interpret the data further, one must consider that the one and threefold rotational amplitudes under s/s polarization can interfere. These one and threefold amplitudes are represented by $d_{11}^{(1)}$ and $d_{11}^{(3)}$ in Eq. 5. Two cases can be expected for a surface with C_s symmetry which follows Eq. 5, one in which the two amplitudes have the same sign and are out of phase by 180° (case I), and one in which the two amplitudes have different signs and are therefore in phase (case II). The resulting anisotropies for these two cases are distinctly different. For case I the polarization which is normal to the steps (the susceptibility χ_{xxx}) is dominant over the other in-plane susceptibilities χ_{yxy} and χ_{xyy} (see Eq. 5). The dominance of χ_{xxx} means that the steps introduce a higher susceptibility in the direction perpendicular to the steps (χ_{xxx}). The step sites result in a stronger asymmetry in the surface potential giving rise to a higher SHG efficiency. An anisotropy consistent with this interpretation was reported on vicinal Si(111) surfaces in which the crystals were cut with an offset in the $[1\bar{1}2]$ direction.^{25, 26} However, quite surprisingly, this seemingly consistent interpretation cannot explain the results in this study.

A comparison of the results in Figs 2(b) and 2(c) with the above discussion shows that in fact the data is most consistent with case II in which the one and threefold amplitudes are in phase. This would suggest from Eq. 5 that the susceptibility perpendicular to the steps is small relative to the other two in-plane susceptibilities χ_{yxy} and χ_{xyy} . The physical interpretation for such relative ordering of the susceptibilities can be seen in Figure 3 which shows a model for the (211) surface. An idealized surface with monoatomic steps and constant terrace width is shown. For surfaces of fcc metals cut towards the $[2\bar{1}\bar{1}]$ direction from the (111) surface the resulting steps have a (100) orientation. Looking carefully at the darkened atoms, it is apparent that a mirror plane exists perpendicular to the $[1\bar{1}\bar{1}]$ direction along the $[1\bar{1}0]$ direction. For every triangle of atoms found on the terrace, there is a triangle of atoms oriented in the opposite direction on the next terrace. This is

a consequence solely of the (100) orientation of the steps and holds true also for steps of multiple atomic height. The reduced susceptibility in the direction perpendicular to the (100) oriented steps is therefore attributed to an almost symmetrical surface potential in this direction.

Such an explanation for the response in terms of a pseudo mirror plane at the steps is consistent with the vicinal Si work described above²⁵ in which the cut is in the $[11\bar{2}]$ direction. This type of a surface which has (111) oriented steps without any mirror plane would result in high susceptibilities normal to the steps and to an SH intensity pattern which is consistent with case I of Fig. 3. This explanation is consistent with both studies. The experiments reported here suggest that the pseudo mirror plane at the steps has a stronger influence on the SH rotational anisotropies than the enhancement due to a stronger asymmetry of the potential at the termination of the crystal lattice in the surface plane.

For the stepped crystal experiments in which s/s polarization is used, no significant potential dependence in the SH intensity was found within the detection limit of these experiments. It is therefore concluded that, as with the unstepped surface, the static electric field at the stepped surface is strictly oriented in the z-direction. In this case no potential dependence in the in-plane contribution to the SH signal is expected nor is it observed. This result is of particular importance to the studies of surface reconstructions in electrochemical environments which are based on detecting symmetry changes. No potential induced symmetry change should be expected from (accidentally prepared) stepped surfaces. With p/s polarization a pronounced potential dependence is observed for the stepped surfaces. Figures 4(a) and (b) show the rotational anisotropy data taken for the (211) surface -0.1 V and -1.0 V, respectively. The rotational amplitudes reflecting again the Cs symmetry of this highly stepped surface were obtained by fitting the data to Eq. 6. Inspection of the amplitudes obtained from the fits show that only those amplitudes involving susceptibilities with z-field direction show significant potential dependence.

Experiments have also been performed on stepped crystals for which the goal has been to determine whether SHG can distinguish between step and terrace sites on the surface by underpotential deposition of Pb^{2+} on these surfaces. These results will be described in more detail

in a later publication. Although lead underpotential deposition has been studied extensively by conventional electrochemical methods, the assignment of the deposition processes to the observed three peaks in the monolayer deposition region continues to be of question. Current/voltage measurements often show one sharp deposition peak which has been associated with monolayer deposition (A_2). This is often accompanied by two small broad peaks on either side of A_2 (conventionally referred to as A_1 and A_3) which are particularly sensitive to surface preparation and have been attributed to defect sites on the surface.²⁷ The SHG studies show that the initial stages of deposition on both types of stepped surfaces involve adsorption at the step sites which lead to an increase in χ_{xxx} due to the lead atom at the step site destroying the pseudo mirror plane and additionally leads to a more asymmetric potential at the termination of the metal in the crystal plane. Both effects are consistent with the observed increase in SH efficiency in this direction. Furthermore it is found that although adsorption at defect sites exhibits a stronger influence on the SH intensity than adsorption on terraces, most of the contributions from the steps (and other defect sites) vanish by interference on the flat Ag(111) surface. All observed features are compatible with the understanding of the anisotropy being due to a global interaction with the whole irradiated surface and not due to specific sites on the surface as postulated by Janz et al.¹³

In summary, the rotational anisotropy of a highly stepped Ag(211) surface and a vicinal Ag(111) surface with a lower density of steps has been examined in perchlorate solutions. The introduction of steps on the metal surface appears to have a strong influence on the SH response similar to what is observed on semiconductor surfaces. All rotational patterns from the stepped crystals are consistent with a C_s symmetry. The existence of a pseudo mirror plane at the steps has a stronger influence on the SH rotational anisotropies than the enhancement due to a stronger asymmetry at the in-plane termination of the crystal lattice. This indicates that the interpretation of the SH response requires consideration of the overall surface structure, instead of just local components such as the step sites.

Acknowledgements: The authors wish to thank Richard Bradley and John Daschbach for scientific discussions and assistance in preparing this manuscript. Financial support from the Office of Naval Research and the National Science Foundation (CHE 8801348 & CHE 9022538) is gratefully acknowledged.

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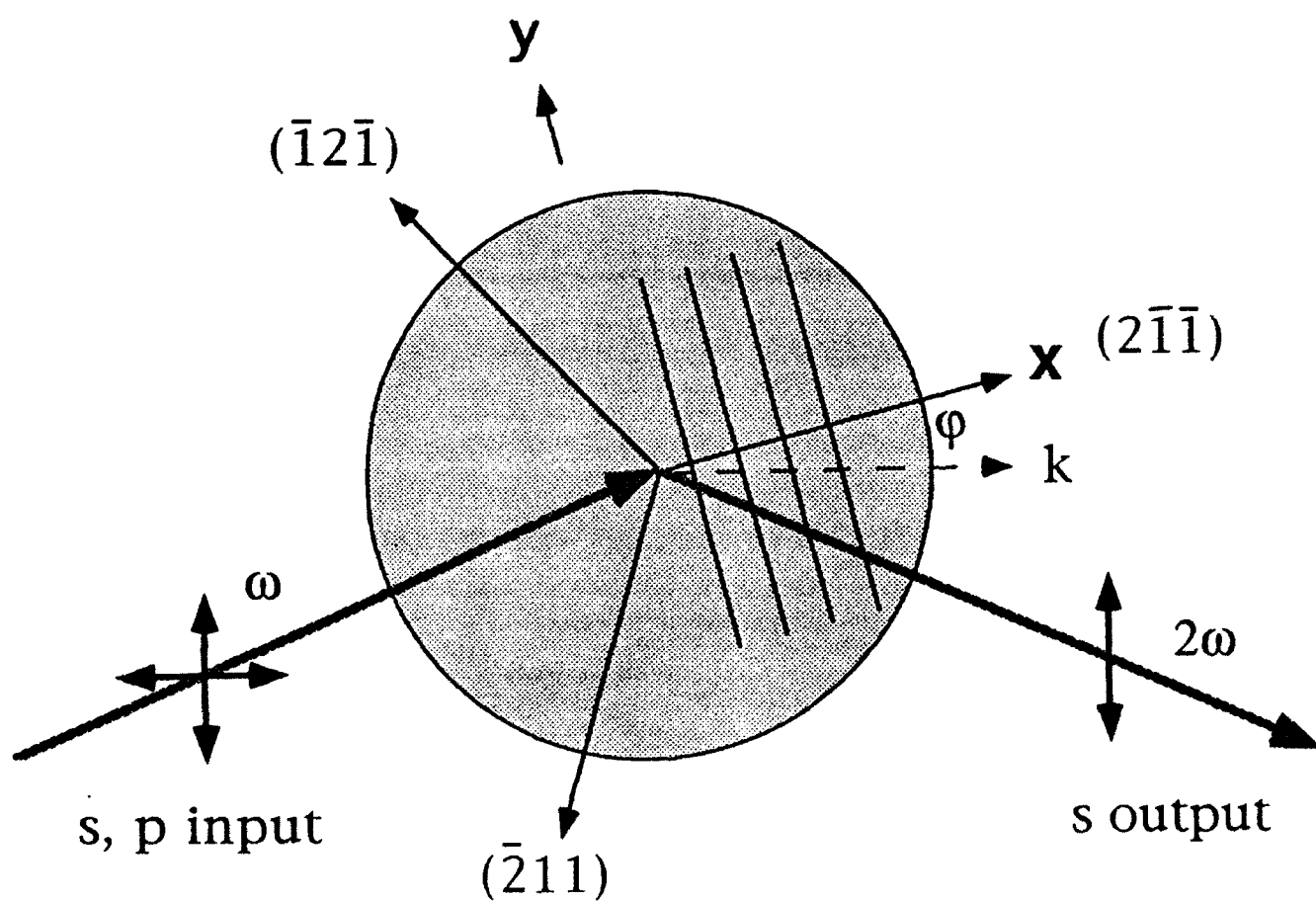
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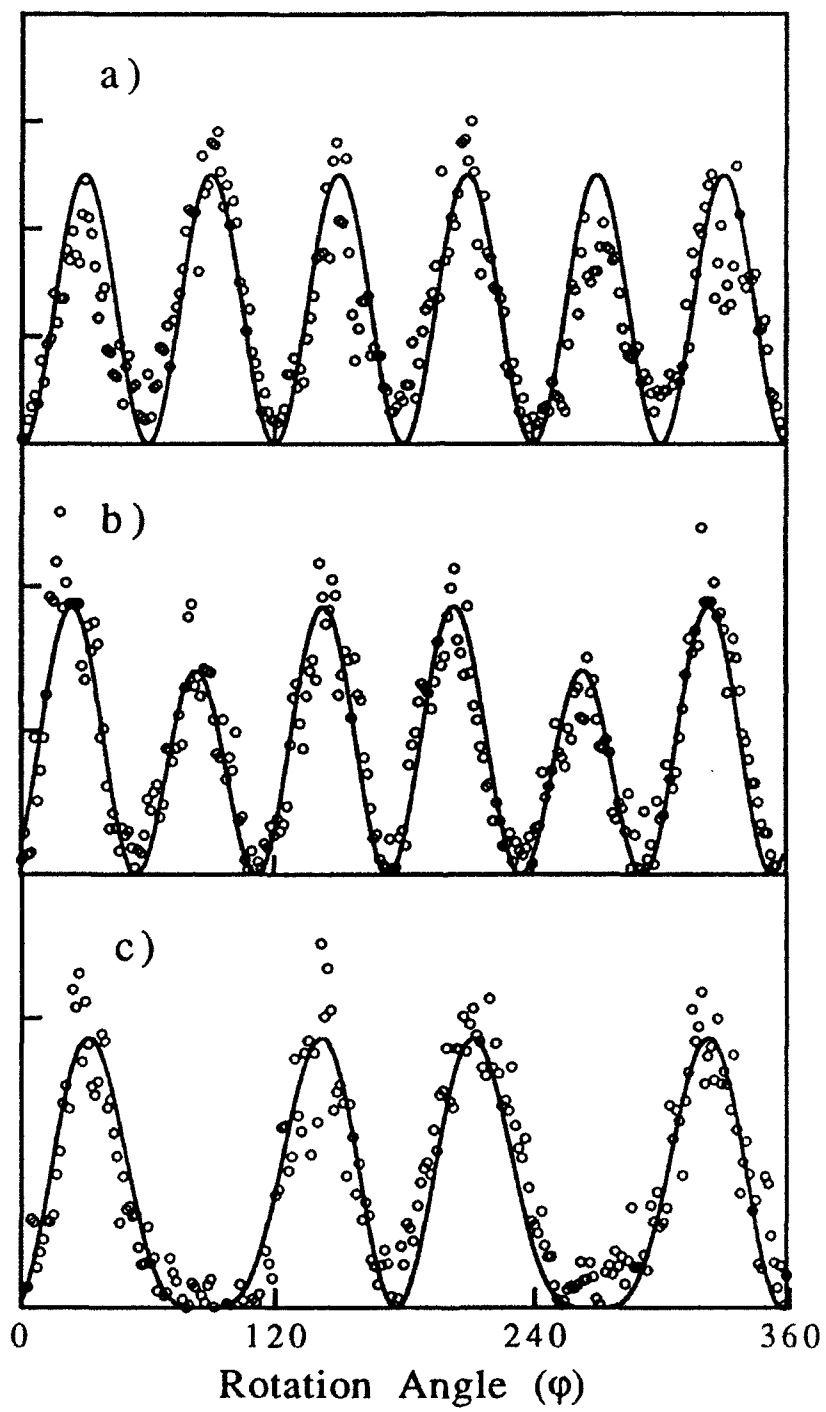
Figure 1. Experimental geometry for the rotational anisotropy measurements. Indicated are the polarizations of the incoming and outgoing beams and the directions on the crystals are shown for the vicinal surface. The rotational angle ϕ is defined as the angle between the direction normal to the steps and the parallel component of the incident wavevector.

Figure 2. SHG intensity from Ag electrodes at an applied potential of -0.5 V as a function of azimuthal angle for s-polarized SHG and s-polarized pump beam. Shown are measurements on (a) the flat Ag(111) surface, (b) the vicinal Ag(111) surface and (c) the Ag(211) surface. Solid lines are fits to Eqs. (3) and (4) respectively, giving the following values in arbitrary units: (a) $d_{11}^{(3)} = 0.5 (\pm 0.1)$, $d_{11}^{(1)} = 0 (\pm 0.005)$, (b) $d_{11}^{(3)} = -0.6 (\pm 0.1)$, $d_{11}^{(1)} = 0.05 (\pm 0.005)$, and (c) $d_{11}^{(3)} = -0.4 (\pm 0.1)$, $d_{11}^{(1)} = 0.4 (\pm 0.1)$.

Figure 3. Idealized model of a (211) surface. The representation is shown to indicate a pseudo mirror plane introduced by the (100) orientation of the steps. The darkened atoms illustrate that for every triangle of atoms found on the terrace, there is a triangle of atoms oriented in the opposite direction on the next terrace.

Figure 4. Rotational anisotropies for p-polarized and s-polarized SHG on the Ag(211) surface at an applied potential of (a) -0.1 V vs. SCE. Values for the rotational amplitudes obtained by fitting the data of Eq. (6) are: (a) $d_{12}^{(1)} + d_{13}^{(1)} = 0.22 (\pm 0.05)$, $d_{14}^{(2)} = -0.18 (\pm 0.05)$, $d_{11}^{(3)} = -0.4 (\pm 0.05)$; (b) $d_{12}^{(1)} + d_{13}^{(1)} = 0.23 (\pm 0.05)$, $d_{14}^{(2)} = -0.03 (\pm 0.05)$, $d_{11}^{(3)} = -0.44 (\pm 0.05)$





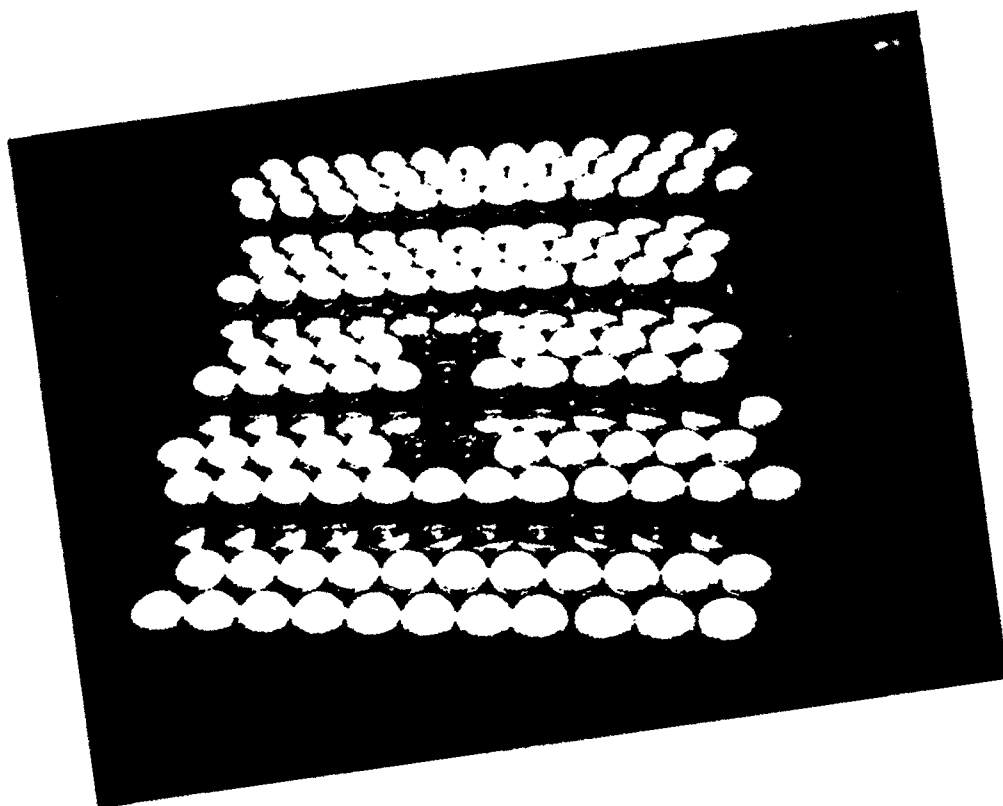


Fig 3

