

Influence of Steps on Second-Harmonic Generation from Vicinal Metal Surfaces

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We demonstrate that the optical second-harmonic (SH) efficiency of a clean metal surface is strongly influenced by the presence of monatomic steps. Vicinal Al surfaces, oriented between 0° and $\pm 10^\circ$ of the (100) plane, were prepared in vacuum; the SH light was produced by picosecond laser pulses with $570 < \lambda < 820$ nm incident at angles up to 67.5° . From the dependence of the SH signal on angle of incidence, wavelength, surface orientation, and oxygen exposure, we conclude that the macroscopic SH polarization of the vicinal Al surface contains comparable contributions from the (100) terraces and the surface steps.

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Surface second-harmonic generation (SSHG) has attracted considerable attention as a powerful optical probe of interfaces between centrosymmetric materials¹ for which the bulk second-order susceptibility vanishes in the electric dipole approximation. This technique has proven to be a valuable probe of clean semiconductor,² metal,³ and insulator⁴ surfaces as well as surfaces with adsorbed atoms and molecules.⁵ For clean metal surfaces, in particular, it also provides a rigorous test of our understanding of the surface electron distribution and the surface linear and nonlinear electrodynamic response. The theoretical understanding of the second-harmonic (SH) response, even from simple "jellium" metals like aluminum, has posed a significant challenge for over 25 years,⁶ and only recently have efforts⁷ advanced to the point where comparisons with experimental results are meaningful.³ However, the theoretical models as well as the interpretation of experimental results have relied on the assumption of a perfectly flat surface, an idealization that does not exist in nature. A nominally flat, low-Miller-index surface always has terraces, steps, and other surface features. Given that the SH response is governed by details of the variation of electron density within 1 nm of the surface,⁷ the validity of comparisons between SH theory and experiment requires a better understanding of the influence of microscopic surface morphology. Here we report the first experimental results for SH generation from clean and oxidized, vicinal Al surfaces and show that the steps on vicinal surfaces can make significant contributions to the SH response.⁸ These results are of fundamental interest to surface scientists because the sensitivity of SSHG to the presence and properties of surface steps opens a new window through which the chemical and structural properties of atomic-scale surface morphology can be investigated.

A surface with a variable step density was prepared

from a cylindrical, 1-cm-diam, single-crystal disk with the [100] axis normal to the plane of the disk. One side of the disk was shaped to form a convex surface. Along the curved surface the angle α between the local surface normal and the [100] axis varied from -10° to $+10^\circ$. The convex surface was mechanically polished to a mirror finish, mounted in an ultrahigh-vacuum chamber with a base pressure of 10^{-10} Torr, and then cleaned using repeated cycles of 1-keV argon-ion bombardment and annealing at 450°C . The LEED pattern from the surface region corresponding to an ideal (100) surface was characterized by a fourfold (100) symmetry. For areas of the surface characterized by $0 < |\alpha| < 6^\circ$ the LEED pattern still possessed a fourfold symmetry but the spots had split into doublets indicating that the local surface consisted of a regular array of steps separated by (100) terraces.⁹ From the separation of the doublets the steps were determined to be approximately 2 Å in height and hence monatomic. If a is the lattice parameter for a fcc crystal, the local density of monatomic steps is $N = |2a/a|$.

For the SH measurements we used a synchronously pumped mode-locked dye laser which produced a train of 3-ps pulses with $570 < \lambda < 820$ nm at a repetition rate of 76 MHz at an average power of 200 mW. A p -polarized beam incident at an angle of $\theta = 22.5^\circ$, 45° , or 67.5° was focused to a $50\text{-}\mu\text{m}$ spot on the sample and SH light was generated in reflection. The filtered SH light was detected using a photomultiplier and conventional photon-counting techniques. Only p -polarized SH light was measured in all experiments.

The SH efficiency from the clean surface was obtained as a function of α by scanning the incident laser spot across the sample along a path defined by the intersection of the plane of incidence and the surface; the plane of incidence was parallel to the (011) plane. Figure 1 shows a typical result observed for a $\lambda = 820$ nm,

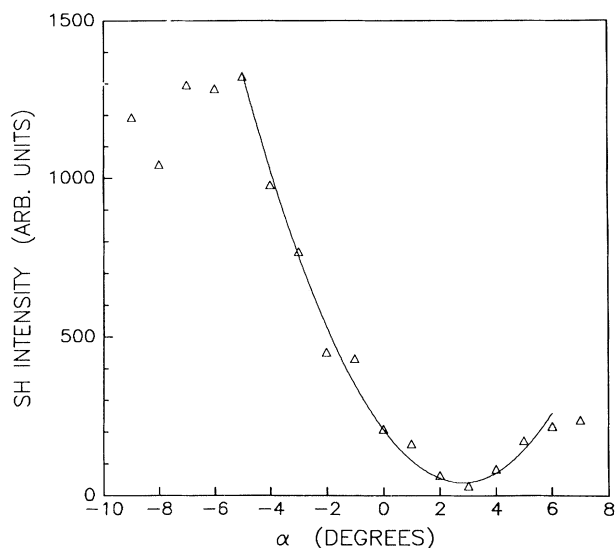


FIG. 1. Second-harmonic (SH) intensity as a function of the angle α between the surface normal and the [100] axis. Data were taken with $\lambda = 820$ nm pulses incident at $\theta = 67.5^\circ$. The triangles are the experimental data points, while the solid curve is the SH intensity calculated using Eq. (4).

$\theta = 67.5^\circ$ beam. We see that as α increases from -6° to 3° the SH intensity decreases monotonically to a minimum after which it increases until $\alpha = 6^\circ$; thereafter the SH signal does not vary with α .

To understand the observed variation of SH intensity with α we have considered a model in which the total SH field is the sum of fields generated by the terraces and by the steps. For small α , one would expect that the field generated by terraces is independent of α since the area of the terraces is independent of α . On the other hand, the field generated by steps is proportional to the number of steps, N . In addition, the presence of a minimum (almost a null) suggests that the relative phase of the two fields changes by (almost) 180° when α changes sign. Note that reversing the sign of α is equivalent to rotating the step by 180° in the surface plane. When α is negative the two contributions add constructively and when α is positive the contributions add destructively. As α increases from 0° , the number of steps increases and a point is reached where the magnitude of the total SH field attains a minimum after which it increases.

The second-harmonic response from the terraces is dominated by the normal component of the SH polarization.⁷ The orientation of the associated SH field is therefore independent of the magnitude and sign of α . On the other hand, one can find components of the SH polarization P^s of a single surface step which satisfy the requirement that they change sign with α . They are

$$P_i^s = \Pi_{iii} E_t E_t + \Pi_{tzz} E_z E_z \quad (1)$$

and

$$P_z^s = (\Pi_{zzt} + \Pi_{ztz}) E_t E_z. \quad (2)$$

Here Π_{ijk} is the SH susceptibility tensor of a step, t denotes the direction tangential to the terrace plane and perpendicular to the step face, and z denotes the direction normal to the terrace plane.

The total polarization density (for p -polarized light) has a linear dependence on α of the form

$$\mathbf{P} = \mathbf{P}^T + |2\alpha/a| \mathbf{P}^s = \mathbf{P}^T + N \mathbf{P}^s, \quad (3)$$

where \mathbf{P}^T is the p -polarized component of the terrace polarization. Since a step polarization P_i^s of the form given in Eqs. (1) and (2) changes sign as α passes through zero, the SH intensity will have the quadratic form

$$I_{2\omega} = I_0 |1 - R\alpha|^2, \quad (4)$$

where the complex quantity αR gives the ratio of the SH field radiated by the steps to that radiated by the (100) terraces for the particular angle of incidence. Equation (3) fits the data in Fig. 1 well for $R = 0.32e^{i0.46}$. The uncertainty in R is approximately 50% due to an uncertainty of $\pm 1^\circ$ in the exact direction of the [100] axis.

Near the edges of the convex sample where $|\alpha|$ is larger than 6° and the SH intensity no longer has a parabolic dependence on α the LEED spots evolve into broad streaks rather than the sharply defined doublets observed at small α . We conclude that the surface structure no longer consists of a regular array of monatomic steps but rather that the surface forms steps of varying height.

Support of the above model for surface SH generation was obtained from experiments in which the SH signal was monitored as the sample was exposed to O_2 at a pressure of 5×10^{-8} Torr. This experiment was carried out for three different geometries. In the first geometry the plane of incidence was set perpendicular to the step edges and a surface with $\alpha = -4^\circ$ was chosen. In the second experiment SH light was generated at a flat (100) Al surface ($\alpha = 0$). In the third geometry $\alpha = -3^\circ$ but the plane of incidence was now set parallel to the step edges. The results of these experiments, which were performed with the same optical beam parameters as for Fig. 1, are shown in Fig. 2. The data obtained for the second and third geometries are virtually the same. The SH in both cases decreases with O_2 exposure until a saturation value is reached after about 300 L [1 L (langmuir) = 10^{-6} Torr s] exposure. Although the experiments of Tom *et al.*⁵ on SH generation from oxidized rhodium supported a model in which the change in SH susceptibility with O_2 exposure depends solely on the fractional surface coverage, our data for Al cannot be analyzed so simply since the oxidation of Al involves both chemisorption and oxide formation.¹⁰ However, our results are consistent with the oxidation studies of Al(100) surface¹⁰ which show that the work function, and hence the surface electronic structure, changes only during the first 300 L of O_2 exposure. In the first geometry used the SH signal dropped by a factor of 2 during the first 50 L of O_2 exposure, after which it

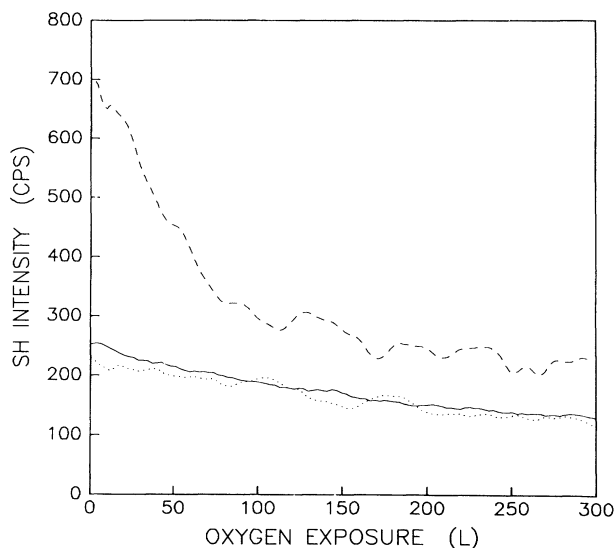


FIG. 2. Second-harmonic intensity ($\theta=67.5^\circ$, $\lambda=820$ nm) from Al as a function of O_2 exposure for a (100) surface (dotted curve), for a stepped surface ($\alpha=-3^\circ$) with the plane of incidence parallel to the steps (solid curve), and for a stepped surface ($\alpha=-4^\circ$) with the plane of incidence perpendicular to the steps (dashed curve).

displayed a similar dependence on exposure as the flat (100) surface. The marked difference between the two results shows that the source of the additional SH signal, obtained when the plane of incidence is perpendicular to the step edges, is physically independent of a flat (100) surface, or a geometry where the plane of incidence is parallel to the step edge.

Previous work has indicated that adsorption on stepped metal surfaces can be strongly enhanced relative to flat low-index surfaces.¹¹ In particular, Testoni and Stair¹² have shown that the sticking probability of O on a stepped Al(111) surface is increased by a factor of 4 over that of a flat Al(111) surface. The observation that the SH signal from a stepped (100) surface decreases 4 times more rapidly with O_2 exposure than the SH from a flat (100) surface is consistent with the interpretation that the additional SH signal is due to the surface steps. Since the oxidation dependence of the SH signal for the second and third geometries is the same, it follows that the SH response in these cases is from the (100) terraces only.

The simplest explanation for the rapid decrease with oxygen exposure of the SH field contribution from surface steps relative to the terrace contribution is that oxygen adsorbs preferentially at sites adjacent to steps. The reduced SH intensity is thought to result because the electrons involved in the metal-oxygen bonds have a much lower SH polarizability than free electrons on a metal surface.⁷ If this were the only effect of chemisorption, one could interpret the SH results in terms of an effective sticking probability for adsorption sites adjacent

to a step. However, adsorbates can also have a profound effect on the morphology of vicinal surfaces.¹³ The LEED patterns from stepped surfaces which were exposed to 40 L of O_2 show streaks of approximately the same length as the separation between LEED spot pairs seen on the clean surface. This suggests that the exposure to O_2 generates steps of variable height since there is no longer a well-defined terrace width. This would reduce the number of steps on the surface and since the steps are no longer identical in structure, the SH response of individual steps need no longer be in phase. Both these effects would alter the observed SH intensity. Thus the decay of the SH response from an oxidized step may involve both the usual change in electronic structure at the step as well as oxygen-induced changes in step morphology.

The variation of the SH signal with θ was also considered for the surface with $\alpha=-3^\circ$ and the plane of incidence perpendicular to the surface steps. For $\theta=67.5^\circ$, 45° , and 22.5° the observed SH intensities had relative strengths of 13:3:1. This set of ratios will of course vary with vicinal angle α since the relative contribution of terraces and steps will vary. When the plane of incidence is rotated to be parallel to the surface steps (i.e., no contribution from surface steps), and for $\theta=67.5^\circ$ and 45° the ratio of intensities is $\approx 10:1$. (No measurable signal was observed for $\theta=22.5^\circ$.) For the three angles the observed results are consistent with theoretical predictions (viz., 1000:70:1) of the SH intensity from a flat jellium surface.⁷ On the other hand, the θ dependence of the SH signal in the first orientation indicates that the step SH response corresponds to the incident fields and SH polarization oscillating parallel to the surface, as expected from the form of Eqs. (1) and (2). For $\theta=22.5^\circ$ the SH intensity is almost entirely due to the step response. Therefore, when the surface is exposed to only 60 L of oxygen, the signal drops by more than a factor of 4, consistent with the results of Fig. 2. Hence for sufficiently small θ it is possible to monitor the SH response of the steps alone.

Results of measurements at different wavelengths show that the SH anisotropy (associated with having the plane of incidence perpendicular or parallel to the steps) decreases monotonically as λ varied from 820 to 570 nm. For $\lambda=570$ nm and $\theta=67.5^\circ$ the step-induced anisotropy was smaller than the experimental uncertainty of $\pm 10\%$. However, the decrease in the anisotropy is partly due to the fact that the SH response from the terraces, which for a jellium metal varies as λ^{-2} ,⁶ has increased by approximately a factor of 2 over the wavelength range considered.

Further experiments are in progress to study the step-induced SH response in aluminum and other metals and semiconductors. Preliminary measurements on vicinal surfaces produced from Cu(111) show that in this "non-jellium" *d*-band metal large variations in the SH intensity are also observed for $|\alpha|$ near 0° .

In conclusion, we have clearly demonstrated that the SH response of steps on a vicinal Al(100) surface can be comparable to that of a flat surface when the surface is oriented as little as 1° away from the (100) plane. The SH polarization at the surface step requires that the incident field has a component perpendicular to the step face. This suggests that the response is clearly related to breaking of inversion symmetry in a direction perpendicular to the step face, leading to new surface susceptibility components. Such components could be expected to be quite large since Thompson and Huntington¹⁴ have indicated that steps strongly modify the local electron distribution and Liebsch and Schaich⁷ have shown theoretically that the SH response of a metal surface is localized to the tail of the electron distribution outside the metal. In addition, Liebsch and Schaich have shown that the SH response exhibits resonant behavior when the SH photon energy corresponds to the work-function energy (in our experiments this occurs for $\lambda \approx 600$ nm). However, the work function of a metal can be reduced by several tenths of an eV for a stepped surface as pointed out by Besocke, Krahl-Urban, and Wagner.¹⁵ The appearance of new, large susceptibility components is not entirely unexpected although a complete theoretical explanation may represent a formidable task. The step-altered SH signal, however, is probably not related to surface-plasmon enhanced effects such as surface enhanced Raman scattering which occurs on rough metal surfaces for roughness features with characteristic length scales of 10–100 nm.¹⁶ Regardless of the details, we have demonstrated here the sensitivity of SH to surface steps and shown that monatomic steps are stable for vicinal angle of less than 6° for Al(100). Finally, we have shown how SSHG can be used to monitor the relative sticking probability of adsorbates at step and terrace sites.

The surprisingly large SH response of steps has two important implications. First, because all crystalline surfaces have steps whose density depends on surface orientation, method of preparation, etc., the interpretation of SH experiments on crystalline surfaces requires careful identification of the contributions to the SH signal. More importantly, because the presence of steps influences the physical and chemical processes occurring at surfaces, surface SH generation can be used as a monitor of such processes and indeed with the appropriate choice of angle of incidence, wavelength, etc., one can preferentially probe step responses alone.

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