Resonant Optical Second Harmonic Generation at the Steps of Vicinal Si(001)

J. R. Power, J. D. O'Mahony, S. Chandola, and J. F. McGilp*

Department of Physics, Trinity College, Dublin, 2, Ireland

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Resonant optical second harmonic generation from vicinal Si(001) and Si(001)-Sb around 3.3 eV is shown to be dominated by electronic states associated with reconstruction of the surface step. The mirror plane perpendicular to the step edge, which is present in the macroscopic surface and in the bulk and terrace crystallographic structures, is absent in the resonant second harmonic response from vicinal Si(001)-(1 × 1)-Sb.

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Optical second harmonic generation (SHG) is known to probe interface structure [1–4], but the microscopic origin and the effective sampling volume of the technique remain unclear. We present spectroscopic SHG studies of well-characterized vicinal Si(001) surfaces which show that the resonant SH response is dominated by electronic states associated with reconstruction of the surface step. We use the 2ω resonance recently found at Si surfaces and interfaces by Daum *et al.* [5] at 3.3 eV, which they attribute to electronic states associated with local strain in the selvedge region, and follow its behavior on adsorbing Sb. Studies of singular surfaces are used to exclude possible bulk and terrace contributions to the resonant SH response.

Singular Si(001) surfaces have a macroscopic *4mm* symmetry, with equal populations of *2mm* (1 × 2) and (2 × 1) domains of Si dimers. Monolayer (ML) coverage of Sb on this surface produces Si(001)-(1 × 1)-Sb and Si(001)-(2 × 1)-Sb under different annealing conditions [6–8]. Vicinal Si(001) surfaces, cut 4° off the [001] plane towards [110], have a macroscopic *lm* symmetry with an x-z mirror plane (defined in Fig. 1), and form predominantly *single domain* (1 × 2) terraces, after suitable heat treatment [9]. Double-height, D_B-type, steps are formed, which favor the domain with the Si dimer bond on the terraces parallel to the step edge [Fig. 1(b)] [10]. Scanning tunneling microscopy (STM) has confirmed a D_B-type step structure, with some buckling (not shown) [11]. From the STM studies it is clear that an x-z mirror plane, present in the macroscopic vicinal surface, is retained in the microscopic structure of the steps. Nonresonant SHG from clean and oxidized vicinal Si(001) surfaces are also consistent with an x-z mirror plane [12,13].

On Sb adsorption followed by annealing, the *terraces* of the vicinal surface first form Si(001)-(1 × 1)-Sb and then the *opposite domain* Si(001)-(2 × 1)-Sb, as shown by low-energy electron diffraction (LEED) and STM [6]. The Sb dimers on the terrace align at 90° to the step edge and to the original Si dimer direction. In contrast to the terrace studies, the *step* structure of this system has not been investigated previously. It is clear, however, that the double-height steps must also undergo a substantial reconstruction on Sb adsorption in order to produce the dominant, opposite (2 × 1) domain. For example, Fig. 1(a) shows a D_A-type step which would favor such a (2 × 1) domain [10].

This is a promising system for testing the sensitivity of resonant SHG to step reconstruction. Experiments were performed in ultrahigh vacuum, using a Ti-sapphire laser, of pulse length 15 nsec, at an incident angle θ of 67.5° to the sample normal. An x-cut quartz Maker fringe SH signal was used for normalization, with the bulk χ_{xxx} for quartz taken as $6.8 \times 10^{-13}\ \mathrm{m\,V^{-1}}$ [14]. The surface SH intensity, for excitation wavelength λ, is given by [15,16]

$$I^s_{2\omega} = (2\pi^2 \sec^2\theta/\varepsilon_0\lambda^2 c)\,|\mathbf{e}^{2\omega}\cdot\chi^s : \mathbf{e}^{\omega}\mathbf{e}^{\omega}|^2 I(\omega)^2, \tag{1}$$

where χ^s is the surface second-order susceptibility tensor and $\mathbf{e}$, the polarization vectors. The latter contain model-dependent Fresnel [17] and local-field factors [18]. We express the surface SH response in absolute units using the square of the matrix element $|\mathbf{e}^{2\omega}\cdot\chi^s : \mathbf{e}^{\omega}\mathbf{e}^{\omega}|$, which is model independent. Possible contributions from bulk, higher order terms are discussed later. Surface and interface quality was determined by LEED and Auger electron spectroscopy. A 3:1 predominance of the Si(001)-(1 × 2) domain, estimated from LEED, was obtained after heat treatment of the vicinal Si(001) samples, giving a

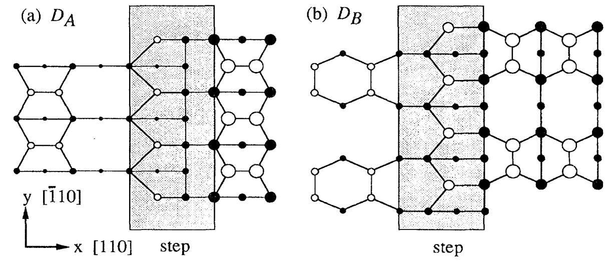

FIG. 1. (a),(b) Top views of "rebound" D_A and D_B double-height steps on vicinal Si(001) [10]. The step region is shaded. Larger circles are used for upper terrace atoms. Open circles are atoms with dangling bonds. Only some of the bonds to underlying atoms are shown.

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9:1 ratio in the SH intensity. 4 ML of Sb were evaporated onto the clean surface at room temperature. The sample was then annealed at 350 °C for 20 min to obtain Si(001)-(1 × 1)-Sb [8], as confirmed by LEED. Further heating to 550 °C for 20 min produced Si(001)-(2 × 1)-Sb [6,8]. The LEED patterns from the vicinal surfaces were sharp, and had the same spot splitting for all three structures, confirming that the regular array of double height steps formed on vicinal Si(001) is maintained on adsorption of Sb.

For excitation at frequency ω, in the x-z or y-z plane of incidence, the variation of s-polarized SH intensity, with input polarization angle α, is of the form [19,20]

$$I^S_{2\omega}(\alpha) = C|\{F\cos^2\alpha + G\sin^2\alpha + H\sin 2\alpha\}I_\omega|^2, \tag{2}$$

where α is measured from the plane of incidence and C is a collection of constants. Input polarizations p, q, and s have $\alpha = 0°, 45°$, and $90°$, respectively. In the x-z plane, tensor components of the general form χ^s_{yjk} are probed (where χ^s_{ijk} refers to the i-coordinate SH field for j, k excitation), because s-polarized output has an SH field vector perpendicular to the plane of incidence. In the absence of any symmetry elements, F depends on χ^s_{yxx}, χ^s_{yxz}, and χ^s_{yzz}, G on χ^s_{yyy}, and H on χ^s_{yxy} and χ^s_{yyz}, as well as the Fresnel and local-field factors discussed above. For excitation in the y-z plane, x and y subscripts are exchanged in the tensor components.

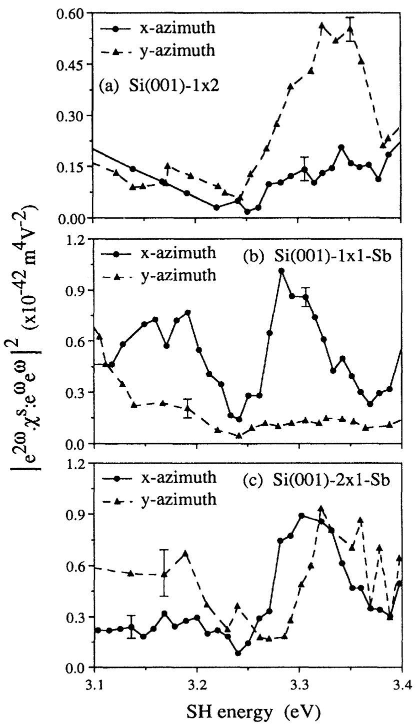

FIG. 2. Variation of q-in/s-out response with SH energy, for *vicinal* (a) Si(001)-(1 × 2), (b) Si(001)-(1 × 1)-Sb, and (c) Si(001)-(2 × 1)-Sb. Note the large in-plane anisotropy in (a) and (b), and the switch of intensity between azimuths.

Figure 2 shows the variation of q-in/s-out response with SH energy, for vicinal (a) Si(001)-(1 × 2), (b) Si(001)-(1 × 1)-Sb, and (c) Si(001)-(2 × 1)-Sb. A large anisotropy in the resonance structure in Figs. 2(a) and 2(b) can be seen, with a dramatic switch of intensity from the x to the y azimuth. The anisotropy is less obvious for Si(001)-(2 × 1)-Sb, appearing mainly as a shift in resonance energy between 3.30 and 3.35 eV. Adsorption of Sb is clearly having a large, and anisotropic, effect on the resonant SH response from the stepped surface. However, possible bulk and terrace contributions must be excluded before the resonant SH response can be identified with step-related electronic states.

We use mirror plane symmetry to interpret the SH signal [21]. Care is required, however, because missing tensor components may not be forbidden because of symmetry, but may simply be too small for detection. Also, with sample rotation patterns obtained at fixed polarization (the most widely used experimental procedure), contributions from different symmetries may be difficult to untangle [22], and this approach may not offer the best way of extracting key information.

The overall SH polarizability of vicinal surfaces is treated as the coherent sum of the terrace and step polarizabilities [12,13,23,24]. For example, the steps on Si(001)-(1 × 2) have lm symmetry, with the x-z mirror plane at 90° to the step edge, while the (1 × 2) terrace has $2mm$ symmetry, also with an x-z mirror plane. When the plane of incidence is aligned with the x-z mirror plane, the s-polarized SH response depends only on χ^s_{yxy} and χ^s_{yyz}, the other tensor components being zero by symmetry. Any s-polarized SH response under these conditions must then vary as $\sin^2 2\alpha$, via H in Eq. (2). Any other *observed* variation in α excludes the plane of incidence being a mirror plane of the surface. This is a strong proof that has not been used previously.

Of the vicinal surfaces in Fig. 3, only Si(001)-(2 × 1)-Sb shows $\sin^2 2\alpha$ behavior in the x-z mirror plane direction. For Si(001)-(1 × 2), the SH response to excitation in the x-z plane shows no resonant enhancement (Fig. 2). A strong non-$\sin^2 2\alpha$ response is observed for excitation in the y-z plane, however, which allows us to exclude a y-z mirror plane in the resonant response of this structure. The absence of a y-z mirror plane is consistent with the STM and nonresonant SHG data discussed above [10–13].

Vicinal Si(001)-(1 × 1)-Sb is dramatically different (Fig. 3), with a resonant non-$\sin^2 2\alpha$ response for excitation in the opposite, x-z plane of incidence. The presence of an x-z mirror plane is excluded at resonance. This mirror plane is present in the macroscopic surface, in the crystallographic structure of the bulk, in any terrace structure with (1 × 1) symmetry, and in the projection of the bulk at the vicinal angle [12,13]. This last factor, arising from the nonsymmetric stacking of atomic planes parallel

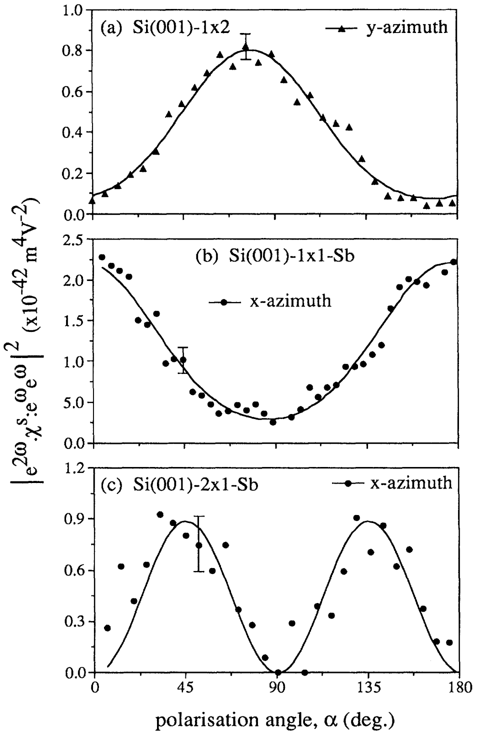

FIG. 3. Variation of s-polarized SH response at 3.30 eV, corresponding to the resonance maxima of Fig. 2, with input polarization angle α for *vicinal* (a) Si(001)-(1 × 2), (b) Si(001)-(1 × 1)-Sb, and (c) Si(001)-(2 × 1)-Sb. The solid lines are least squares fits by Eq. (2). Note the absence of $\sin^2 2\alpha$ behavior in (a) and (b), showing that there is no y-z mirror plane in the Si(001)-(1 × 2) response, or x-z mirror plane in the Si(001)-(1 × 1)-Sb response. The opposite azimuths have a response at least a factor of 10 smaller.

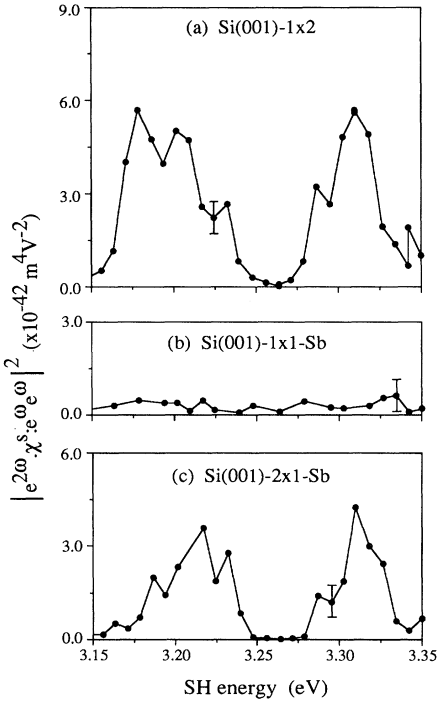

FIG. 4. Variation of p-in/p-out SH response with SH energy, for *singular* (a) Si(001)-(1 × 2), (b) Si(001)-(1 × 1)-Sb, and (c) Si(001)-(2 × 1)-Sb.

to the macroscopic surface, has recently been calculated [25] to produce the dominant contribution to the SH response from stepped Al surfaces [24]. We can exclude all these possible contributions by symmetry. Only step-related electronic states remain to produce a resonant SH response lacking an x-z mirror plane.

Further evidence comes from the size of the signal. Bulk SHG from Si(001) samples, using p-in/p-out polarization at 1064 nm excitation, has been measured at less than 10^{-43} $\mathrm{m}^4\,\mathrm{V}^{-2}$ [16]. In Fig. 4, the isotropic SH response from *singular* Si(001)-(1 × 2) and Si(001)-(2 × 1)-Sb, using p-in/p-out polarization, is a factor of 50 higher at resonance than the bulk response. Also, the q-in/s-out response in Fig. 2 is about a factor of 10 higher than the bulk p-in/p-out signal. Even a generous error estimate of 50% in the absolute SH response does not affect the conclusion that the bulk contribution is negligible at resonance.

Returning to the terrace contribution to the vicinal response, this was shown, by symmetry, to be negligible for vicinal Si(001)-(1 × 1)-Sb. The singular samples can be used to exclude a possible terrace response from all the vicinal structures. No signal from the corresponding singular surfaces was seen, under our excitation conditions, using the q-in/s-out configuration. This places an upper limit of 1×10^{-43} $\mathrm{m}^4\,\mathrm{V}^{-2}$ on the SH response, and any significant terrace contribution in Figs. 2 and 3 is excluded.

We have now shown that the dramatic changes in the SH response in Figs. 2 and 3 must be associated with the steps, and their *local* reconstruction on adsorption of Sb (LEED shows that the average step height and separation are unaffected by Sb adsorption). The second-order perturbation theory expression for χ^S_{ijk}, within the dipole approximation, may become dominated by terms of the form $\langle g|i|n\rangle/(2\omega - \omega_{ng} + i\Gamma_{ng})$, when the denominator becomes small at a 2ω resonance. The dipole moment transition matrix element $\langle g|i|n\rangle$ is along the i coordinate between the electronic ground state g and an excited state n, with Γ^{-1}_{gn} being a relaxation time [15]. The effective SH sampling volume will then be determined by matrix elements that connect electronic states at resonance. If these states are localized at the step edges, then the symmetry behavior, the almost complete anisotropy, the small width of the resonances, and the sensitivity to reconstruction at the step edge are all readily understood.

Possible models of the Sb-induced step reconstructions will be discussed elsewhere [26]. Here we only point out that the rebonding in the D_A and D_B step structues of Fig. 1 produces strain along the x azimuth. The Si(001)-(1 × 2) results showing χ^s_{xjk} components to be dominant (Figs. 2 and 3) are consistent with the hypothesis of Daum *et al.* [5] that the 2ω resonances around 3.3 eV are related to local strain. However, χ^s_{yjk} components are dominant for Si(001)-(1 × 1)-Sb, and y-azimuth strain would not appear to be consistent with a D_A step.

Finally, we mention an apparent conflict between the p-in/p-out data of Daum *et al.* [5], who found a single large resonance between 3.15 and 3.40 eV, and the p-in/p-out data of Lüpke, Bottemley, and van Driel [13] (mentioned above), at 3.24 eV, who found negligible resonance and a bulk response comparable in size to that of the (001) surface. In Fig. 4, the p-in/p-out resonance of Daum *et al.* [5] is shown to be resolved into two resonances at 3.20 and 3.31 eV, of width 0.04 eV. The energy chosen by Lüpke, Bottomley, and van Driel lies between the two resonance peaks, removing the apparent conflict. In addition, their off-resonance data are quite different from our resonance results, both in their symmetry behavior and in the relative size of the various tensor components [13]. This contrasting behavior provides further evidence that the 3.3 eV resonant response from vicinal Si(001) surfaces is dominated by electronic states localized at the steps. A detailed description of these states and their SH response must await realistic calculations, which will remain difficult for such surfaces. Symmetry-related arguments, of the kind that have been presented, are especially valuable in these cases.

In conclusion, resonant SHG has revealed an adsorbate-induced local reconstruction of atomic steps on Si(001). This highly local response can be understood if the resonant electronic states are localized at the steps. Such a response may be generally expected when resonant SHG involves localized electronic states.

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*To whom all correspondence should be addressed.

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