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Second harmonic response of the Si(111)7×7 surface

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ABSTRACT

Optical second harmonic generation spectra have been experimentally obtained from a clean Si(111) 7×7 in two different polarization configurations isolating the rotational anisotropic and isotropic contributions. The energy of the fundamental photon is varied from 0.8 eV to 2.5 eV. For comparison, we also use a microscopic formulation based on the semi-empirical tight binding method to evaluate the nonlinear surface susceptibility tensor $\chi(2\omega)$. Good agreement between theory and experiment is obtained with respect to the number of resonances, their position in energy, and surface or bulk character.

1. Introduction

We compare experimental and theoretical optical second harmonic generation (SHG) spectra of one of the most fascinating of all semiconductor surfaces, the Si(111) surface with a 7×7 reconstruction. The unit cell of this huge reconstruction has 49 atoms instead of the single atom of the simple 1×1 reconstruction. As it is well known the bulk dipolar contribution to the second harmonic susceptibility tensor $\chi(2\omega)$ is identical to zero in a centrosymmetric system. However, on the surface such a dipolar contribution is finite and thus SHG is a very powerful tool to study surface phenomena,[1,2] and its application to Si(111) 7×7 is no exception.

The 7×7 reconstruction of the Si(111) surface leads to a number of localized surface states that can be probed by surface sensitive optical techniques. Due to the inherent surface sensitivity optical SHG has proven to be a very sensitive technique for studies of surface states of this system as it was demonstrated by Heinz et al.[3] in the real time monitoring of the transition from 2×1 to 7×7 reconstruction during sample annealing. Over the years several spectroscopic studies showing broad spectra of transitions below the onset of interband transitions involving bulk like bands have been presented.[4,5,6,7,8] More recently, time resolved experiment has been used to study electron dynamics of the 7×7 surface states. In combined time resolved SHG and two-photon photoemission experiments Voelkmann et al.[9] and Mauerer et al.[10] obtained information about ultrafast carrier dynamics in the system of dangling bond electrons. McGuire et al.[11] used SHG transient spectral hole burning to determine homogeneous linewidths of surface excitations. Interpretations of SHG spectra have mostly been based on information about surface states obtained by other techniques (e.g. photoemission), symmetry properties of the states, and perturbation of the surface, e.g. by hydrogen or oxygen adsorption. Though linear differential surface reflectance measurements have shown several surface features in the range from 1 to 5 eV,[12] a direct comparison to SHG spectra has not been straight forward due to the different selection rules. Thus, the SHG response of the (111) surface is anisotropic, giving rise to an in-plane polarization that varies with the azimuthal rotation of the surface. It is this rotationally anisotropic contribution to SHG that so far has been used to identify surface contributions to SHG[3–8].

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[1] G. Lüpke, Surface Science Reports **35**, 75 (1999).

[2] M.C. Downer, B.S. Mendoza, and V.I. Gavrilenko, Surface and Interface Analysis **31**, 966 (2001).

[3] T.F. Heinz, M.M.T. Loy, and W.A. Thomson, Phys. Rev. Lett. **54**, 63 (1985).

[4] U. Höfer, Appl. Phys. A **63**, 533 (1996).

[5] K. Pedersen and P. Morgen, Phys. Rev. B **52**, R2277 (1995).

[6] K. Pedersen and P. Morgen, Phys. Rev. B **53**, 9544 (1996).

[7] K. Pedersen and P. Morgen, Surf. Sci. **377–379**, 393 (1997).

[8] T. Suzuki, Phys. Rev. B **61**, R5117 (2000).

[9] C. Voelkmann, M. Mauerer, W. Berthold, and U. Hfer, Phys. Stat. Sol. (a) **175**, 169 (1999).

[10] M. Mauerer, I. Shumay, W. Berthold, and U. Höfer, Phys. Rev. B **73**, 245305 (2006).

[11] J.A. McGuire, M.B. Raschke, and Y.R. Shen, Phys. Rev. Lett. **96**, 087401 (2006).

[12] R. Alameh and Y. Borensztein, Surface Science **251–252**, 396 (1991).

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In this work theoretical calculations of the SHG spectra of the Si (111) 7 × 7 surface are compared to new experiments recorded over a broad spectral region for both the isotropic and the anisotropic polarization combinations. Due to the large unit cell the number of theoretical treatments of linear and nonlinear optical properties of this surface is very limited. Semi-empirical tight-binding calculations were used by Noguez et al.[13] to describe optical transitions in the 7 × 7 system. A broad range of transitions among surface states and surface state to bulk band transitions was identified and compared to experimental scanning differential reflection spectra.[14] Several studies have been made of Si(111) surfaces in reconstructions with smaller unit cells such as 1 × 1 and 2 × 1.[15,16] In a combined experimental and theoretical study of Si(111)(1 × 1)H a density functional theory in the local-density approximation has been used to describe resonances in the nonlinear response. Good agreement concerning spectral features and to some extent also absolute intensities was obtained.[17] More recently, Stamova and Rebentrost calculated the linear and SHG optical response for an ideal Si(111) surface including the Coulomb excitonic interaction within the semi-empirical tight binding (SETB) approach.[18] They find that the surface related SHG resonances are mildly modified by the excitonic effects. However, the computational burden that the 7 × 7 surface imposes is such that it is only feasible to perform a microscopic calculation within the SETB approach without excitonic effects. Indeed, we find that the slab required to represent the surface must contain 28 atomic layers to obtain converged spectra. This means 1356 atoms, and thus, an *ab-initio* calculation would be extremely difficult. From the experimental side, tunable lasers readily allow a full spectroscopic study of some of the most relevant electronic transitions of this surface. Comparison of experiments with theory allows us to draw interesting conclusions regarding the surface state electronic transitions of this surface.

In this article, in Section 2 we first review the morphological characteristics of the reconstructed surface and its implication on the symmetry of the SH susceptibility tensor $\chi(2\omega)$. In Section 3 we review the equations required to calculate the SH radiated efficiency, and in Section 4 we give some of the experimental details. Then, in Section 5 we compare the theoretical results with the experiments, and conclusions are given in Section 6.

2. Symmetry of the Si(111) 7 × 7 surface

We follow the Dimer–Adatom–Stacking (DAS) fault model of Takayangai et al.[19] to describe the atomic arrangement of the surface, from which SHG is calculated. In Fig. 1, we show the DAS model that has the following morphology. The unit cell of the first atomic plane has only 42 atoms, instead of 49, due to a fault in the stacking of the planes. On top of this plane, there are 12 adatoms (ADs) that saturate 36 of the 42 dangling bonds (DBs) of the atoms of the first plane denoted by a cross in Fig. 1. The remaining 6 atoms of the first plane with unsaturated dangling bonds are called the rest-atoms (RAs). Some atoms from the second plane are displaced laterally in such a way that they form a bond called a dimer. In short, the DAS model has 6 corner adatoms, 6 center ADs, 6 rest-atoms and 1 corner-hole that give 19 DBs, plus 9 dimers and the stacking fault along the minor diagonal of the unit cell which divide the cell in two subunits, one faulted and one unfaulted. The molecular dynamic *ab-initio* calculations have shown that the DAS model is energetically favorable compared to other models.[14,20] The atomic positions are taken from these *ab-initio* calculations.[21] Below the fourth atomic plane the atomic positions are bulk like.

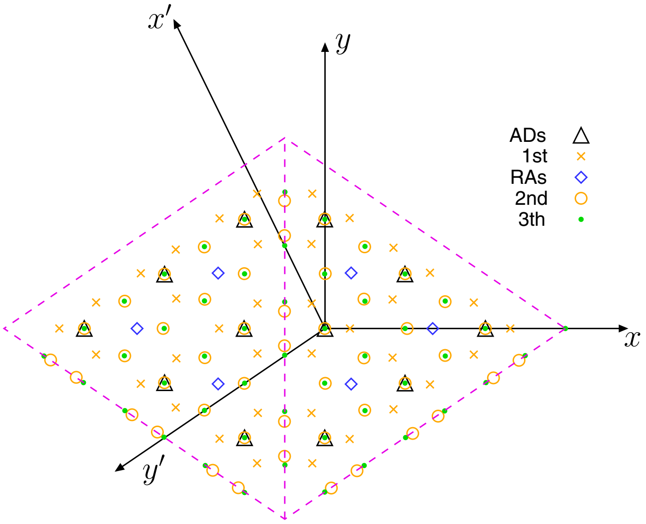

Fig. 1. We show the three first planes plus the adatoms (ADs) for a Si(111)7 × 7 surface, according to the Dimer–Adatom–Stacking (DAS) fault model[19]. The 36 atoms denoted by crosses (labeled "1st"), along with the 6 rest-atoms (RAs), belong to the first plane. The *xy* axes are rotated by 120° with respect to the *x′y′* axes. The rhomboid with dashed lines denotes the unit cell, and the minor diagonal can be seen as a dashed vertical line. Note that with respect to the ADs, the RAs do not satisfy the 120° rotational symmetry. The same is true for the other planes.

For an ideal Si(111) 1 × 1 surface, $\chi(2\omega)$ satisfies the following symmetry relationship,

$$\chi_{xxx} = -\chi_{yyx} = -\chi_{xyy}, \tag{1}$$

where these components are different from zero due to the fact that the *zy* plane is not a mirror plane, and there is a 120° symmetry operation at this surface. That is, rotating the coordinate system by 120° gives exactly the same environment for any given atom of the unit cell (only one atom for the 1 × 1). This environment involves not only the atoms on the same plane, but also, and more importantly, the atoms on the neighboring planes. If we take any of the atoms on the first three planes or the ADs, we see from Fig. 1 that this 120° symmetry is not satisfied. The environment due to the atoms on the planes above or below makes the original coordinate system different from the rotated one. Thus, although the *zy* plane is still not a mirror plane, the restriction of Eq. (1) should no longer hold. Then, in general for a reconstructed DAS Si(111) 7 × 7 surface, we have that the following relationship holds

$$\chi_{xxx} \neq \chi_{yyx} \neq \chi_{xyy}. \tag{2}$$

This fact implies that the symmetry shown by the SH reflected efficiency factor, $\mathcal{R}(2\omega)$, in its azimuthal rotation could be different from the six-fold symmetry of the ideal 1 × 1 unit cell. However, as shown experimentally in Ref.[3], the macroscopic symmetry of the 7 × 7 reconstructed surface is that of the 1 × 1 unit cell. This means that the microscopic components of $\chi(2\omega)$ given in Eq. (2) should be averaged

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[13] C. Noguez, A.I. Shkrebtii, and R. Del Sole, Surf. Sci. **331–333**, 1349 (1995).

[14] C. Noguez, C. Beitia, W. Preyss, A.I. Shkrebtii, M. Roy, Y. Borensztein, and R. Del Sole, Phys. Rev. Lett. **76**, 4923 (1996).

[15] V. Gravilenko and F. Rebentrost, Appl. Phys. A **60**, 143 (1995).

[16] H. Sano, G. Mizutani, W. Wolf, and R. Podluoucky, Phys. Rev. B **66**, 195338 (2002).

[17] J.E. Mejía, B. Mendoza, M. Palummo, G. Onida, R.D. Sole, S. Bergfeld, and W. Daum, Phys. Rev. B **66**, 195329 (2002).

[18] M. Stamova and R. Rebentrost, Phys. Status Solidi B **247**, 2012 (2010).

[19] K. Takayanagi and Y. Tanishiro and S. Takahashi and M. Takahashi, Surf. Sci. **164**, 367 (1985).

[20] K. D. Brommer and M. Needels and B. Larson and J.D. Joannopoulos, Phys. Rev. Lett. **68**, 1355 (1992).

[21] We thank Dr. Cecilia Noguez for allowing us to use her atomic position of Si(111) (7×7). D.R. Alfonso, C. Noguez, D.A. Drabold, S.E. Ulloa, Phys. Rev. B 54, 8028 (1996).