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OPTICAL SECOND-HARMONIC GENERATION FROM SEMICONDUCTOR SURFACES

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ABSTRACT

The nonlinear process of second-harmonic generation has proved to be a powerful tool for the investigation of surfaces and interfaces of centrosymmetric media. In this paper, a brief survey of the development and applications of the technique for the case of semiconductors is presented.

INTRODUCTION

For centrosymmetric materials, the nonlinear optical process of second-harmonic generation (SHG) has been found to exhibit a high degree of sensitivity to the atomic structure and composition of surfaces and interfaces. This surface-specific character of the SH radiation arises from the selection rule that prohibits a second-order nonlinear response in centrosymmetric media within the dipole approximation. Only in the region of a surface or interface, where the inversion symmetry of the bulk material is broken, can a strong nonlinear polarization be produced. In the paper, a brief review of some recent applications of the SH technique in investigations of semiconductor surfaces will be given. Particular emphasis will be placed on information concerning the symmetry and ordering of the surface region implicit in the polarization dependence of the SHG process. For a more general overview, see Ref. 1.

EARLY INVESTIGATIONS

The initial demonstration of the possibility of generating the SH of optical radiation with laser excitation was performed in 1961 by Franken and coworkers [2] using a non-centrosymmetric quartz crystal. In the following few years, the SHG process in centrosymmetric materials was the subject of considerable study. The effect was first observed in metals by Brown et al. [3] and, shortly thereafter, in centrosymmetric semiconductors by Bloembergen et al. [4,5] In these early investigations, a framework for treating the nonlinear process was developed. [5,6] An intense beam of pump radiation at frequency ω gives rise to collimated radiation at frequency 2ω propagating in the forward and reflected directions from the surface of the sample. The nonlinear process is essentially instantaneous and exhibits a quadratic relation between the intensity of the fundamental and harmonic radiation.

In regard to the origin of the nonlinearity for centrosymmetric media, it was recognized that a strong nonlinear response could arise in a very thin (~ Å) surface layer and that only a weak nonlinear response associated with magnetic-dipole and electric quadrupole terms would be present in the bulk of the material. These higher-order bulk contributions, proportional to electric-field gradients, are allowed even in a centrosymmetric medium. Despite the considerably smaller magnitude of the effective nonlinear polarization anticipated from the bulk nonlinearity compared with that of the asymmetric surface region, the magnetic-dipole and electric-quadrupole terms are present in a much larger volume and, hence, may still lead to a significant contribution to the total SH signal. [4,7] In the analytic treatment of the surface nonlinear response, the initial work placed emphasis on the strong electric-quadrupole terms associated with the abrupt change in the normal component of the electric field occurring at the surface. The influence of the altered material properties in the surface region was not considered in detail, although the effect of strong applied dc electrical fields was noted. [8] Experimental results for surfaces under ambient conditions showed little apparent sensitivity to surface treatment, in accordance with theoretical developments based primarily on the bulk material parameters. In subsequent studies performed under more controlled conditions, [9,10] the sensitivity of the SH response to the atomic properties of the surface was observed. Chen et al. [10] discovered that the SH signal from a clean Ge surface increased ten-fold upon deposition of a monolayer of Na. This effect, explained in terms of the higher nonlinear polarizability of the metallic Na surface with respect to that of a semiconductor, gave the first clear indication of the potential of the SH technique to reveal the characteristics of surfaces and interfaces on the level of a single monolayer.

SHG AS A SURFACE PROBE

The development of the SHG process as a tool for investigations of the properties of surfaces and interfaces was sparked by observation of a dramatic change in SHG efficiency from a silver surface in an electrochemical environment accompanying the adsorption of monolayers of various molecular species. [11] Although the SH signal was enhanced by the special electromagnetic properties of the roughened surface in the initial work, it was recognized that a monolayer of aligned non-centrosymmetric molecules having a typical nonlinear polarizability should be readily detectable. Subsequent studies on adsorbed molecular layers demonstrated the possibility of surface-specific spectroscopy by SHG.[12] Such measurements are accomplished by scanning the pump laser frequency and monitoring the resonant SH response when either the fundamental or harmonic frequency coincides with electronic transitions in the material system. The same principles are clearly applicable for electronic transitions in semiconductor surfaces and adsorbate-covered semiconductor surfaces, but no systematic studies have yet been performed.

The dependence of the SHG process on the polarization of the electric fields and on rotation of the sample about the surface normal has, on the other hand, been investigated for both molecular monolayers and semiconductor surfaces. From these data, the tensor character of the nonlinear susceptibility of the material can be determined. When the nonlinear response is dominated by that of aligned molecular adsorbates, the relative strength of the different tensor elements of the nonlinear susceptibility can be used to infer molecular orientational parameters, provided that at least partial information on the molecular nonlinearity is available. [13] In the case of semiconductor crystals, the symmetry properties of the SH response should reflect the long-range ordering of the crystal and of the surface of the crystal. This behavior was indeed manifest in the experimental studies of SHG from centrosymmetric semiconductors reported by Guidotti et al. [14] and Tom et al. [15] in 1983. In these works a marked dependence in the SH efficiency was seen from oxidized Si and Ge surfaces as a function of crystallographic face and of rotation of a given face about its surface normal. This strong anisotropy in the SHG process stands in contrast with usual linear optical properties, which are dominated by an isotropic bulk response. [16] Before continuing the discussion of SH studies of semiconductors, we present some the basic formalism describing the second-order nonlinear response of a centrosymmetric medium.

Symmetry Analysis

The dependence of the SH response on crystal face and orientation can be understood directly in terms of a symmetry analysis of the bulk and surface contributions to the nonlinear process. [15,17,18] The nonlinearity of the surface region (where the atomic structure of the material is perturbed from the bulk or strong electric field gradients exist) can be modeled as a sheet of polarization. The nonlinear susceptibility $\chi_s^{(2)}$ relates the electric field vector $\mathbf{E}(\omega)$ at the surface to the induced (effective) nonlinear source polarization in the surface layer:

$$[P_s^{NLS}(2\omega)]_i = \Sigma_{j,k}\ [\chi_s^{(2)}]_{ijk}\, E_j(\omega)\, E_k(\omega). \tag{1}$$

The third-rank tensor $\chi_s^{(2)}$, expressible formally by second-order perturbation theory as an appropriate sum of products of matrix elements of the interaction Hamiltonian and the current operator,[19] is determined by the electronic properties of the surface of the material. The symmetry properties of $\chi_s^{(2)}$ will, of course, reflect those of the surface region itself. As for the bulk contribution to the SHG process, we can write the nonlinear source polarization arising from magnetic-dipole and electric-quadrupole terms in the form

$$[P_b^{NLS}(2\omega)]_i = \Sigma_{j,k,l}\ [\chi_q^{(2)}]_{ijkl}\, E_j(\omega)\, \nabla_k\, E_l(\omega). \tag{2}$$

Here the symmetry properties of the fourth-rank tensor $\chi_q^{(2)}$ will be determined by those of the bulk material.

The forms of the third- and fourth-rank tensors $\chi_s^{(2)}$ and $\chi_q^{(2)}$ for a given symmetry class are well known. [19] For the bulk properties, the most interesting case is that of the m3m symmetry found in the diamond structure of Si and Ge crystals. Although the dominant linear optical response for a material with m3m symmetry is isotropic, the fourth-rank tensor $\chi_q^{(2)}$ exhibits anisotropic behavior. Employing the previously established notation [5] for the isotropic components of the tensor, we can express Eq. (2) as [15]

$$[P_b^{NLS}(2\omega)]_i = (\delta - \beta - 2\gamma)(\mathbf{E}\bullet\nabla)E_i + \beta E_i(\nabla\bullet\mathbf{E}) + \gamma\nabla_i(\mathbf{E}\bullet\mathbf{E}) + \zeta E_i \nabla_i E_i. \tag{3}$$

The coefficients β, γ, δ, and ζ are simply proportional to elements in $\chi_q^{(2)}$, but written in such a way as to indicate the isotropic character of the terms associated with β, γ, and δ and the anisotropic character of the term in ζ. It should be noted that for a homogeneous medium, no contribution of the form $E_i(\nabla\bullet\mathbf{E})$ is present, since $\nabla\bullet\mathbf{E}$ vanishes; Maxwell's equations also imply that the first term in Eq. (3) disappears for excitation by a single plane wave. Certain simplified expressions have been given for the bulk nonlinearity. In the low-frequency limit, it is predicted that the nonlinear response will be isotropic; within a closure approximation, the magnitude of the nonlinearity can then be related to the linear dielectric constant of the medium. [5] For finite frequencies, a formula for the bulk nonlinear susceptibility has been developed based on a bond polarizability model.[20] This model predicts comparable tensor elements for the isotropic and anisotropic response.

The properties of the surface nonlinear susceptibility $\chi_s^{(2)}$ are not governed solely by the nature of the bulk crystal, but reflect the condition and cut of the surface itself. Our only general guideline is that the symmetry group of a surface should be a subgroup of that of the bulk. Table I summarizes the tensor structure of $\chi_s^{(2)}$ for all symmetry classes consistent with long-range translational order in the surface plane and an assumed asymmetry with respect to the surface normal. It can be seen that only for surfaces with 4mm and 6mm symmetry is the SH response indistinguishable from that of an isotropic surface (with inversion symmetry in the plane). Development of a detailed microscopic theory for predicting the magnitude of the symmetry-allowed elements of $\chi_s^{(2)}$ has been limited primarily to work on molecular adsorbates [21] and to model metal surfaces. [22] Progress towards a complete theoretical formulation of the microscopic origin of the nonlinearity of semiconductor surfaces or, more generally, of surfaces exhibiting anisotropy [23] would be highly desirable.

Table I. Number of nonzero and independent elements of the surface nonlinear susceptibility tensor $\chi_s^{(2)}$ for SHG from crystal faces of differing symmetry.

Surface Symmetry	Nonzero elements of $\chi_s^{(2)}$ for SHG	Independent elements of $\chi_s^{(2)}$ for SH
1	27	18
m	14	10
2	13	8
2mm	7	5
3	19	6
3m	11	4
4	11	4
4mm	7	3
6	11	4
6mm	7	3

Oxidized Semiconductor Surfaces

The theory outlined above, coupled with appropriate choices for the symmetry of the surface, was capable of reproducing the experimental data. [15,17,18] In particular, for oxidized Si(100) surfaces, the data were reproduced assuming a surface with 4m symmetry. In this case, the anisotropic response arises only from the bulk material and the bulk coefficient ζ can be determined. For oxidized Si(111) surfaces, 3m symmetry is expected; both the surface and bulk regions then contribute to the anisotropic SH response. From measurements on both crystal faces, it was possible to compare the relative importance of the surface and bulk anisotropic terms for SHG. The Si(111) surface with a native oxide gives rise to roughly comparable surface and bulk contributions to the SH radiation [15] under pump excitation at a wavelength of 532 nm.

The strong dependence of the SHG process on crystal structure and its instantaneous response make the technique especially appealing for studies of phase transitions occurring on short time scales. This notion was beautifully illustrated in the work of Shank, Yen, and Hirlimann. [24] In their experiment, an intense subpicosecond light pulse served to induce melting of an oxidized Si(111) substrate. The SH radiation from an attenuated probe pulse was then recorded as a function of delay time. The anisotropy in the SH response was found to vanish on the time scale of 1 psec, which was taken as indicative of the time required to melt the crystal.[25] Recent advances in these studies include measurements of melting of Si(100) surfaces. [26] For this case, the anisotropic response can arise only from the bulk material, eliminating any ambiguity concerning the spatial region (surface or near-surface bulk) responsible for the dependence of the SH signal on crystal orientation.

Clean, Reconstructed Semiconductor Surfaces

The relationship between the atomic arrangement in the surface region and the polarization and orientation dependence of the SH radiation is clearly illustrated for clean, well-ordered crystal surfaces in ultrahigh vacuum. Properties of such reconstructed surfaces, in which the atomic positions have been altered in order to lower the energy associated with bonds broken in forming the surface, are naturally of central importance in surface science. For the Si(111) surface, either of two reconstructions exist: the metastable Si(111)-2x1 structure (produced by cleaving the bulk crystal) and the equilibrium Si(111)-7x7 structure. Both of these reconstructed surfaces have been probed by the SH technique [27] Very dissimilar polarization dependences for the SHG process were observed in the two cases. Since the bulk structures are identical, we can conclude that the surface contribution to the SH radiation is strong and reflects the differing electronic structure of the two reconstructions. Indeed, analysis of the polarization dependences indicated that the Si(111)-7x7 surface had the full 3m symmetry of the bulk crystal, while the symmetry of the Si(111)-2x1 surface was lowered to that of a single mirror plane (determined by the cleavage direction). The existence of the mirror symmetry planes could be verified to high accuracy by a nulling technique. The measurement is accomplished by examining the SH reponse for fundamental and harmonic electric field vectors polarized perpendicular to the possible mirror plane. For the case of complete symmetry, no SHG is allowed. The implications of these precise symmetry determinations on models of the surface structure, particularly for the Si(111)-2x1 reconstruction, are discussed in Ref. 26.

The difference in symmetry properties of the Si(111)-2x1 and 7x7 reconstructions could be exploited to investigate the Si(111)-2x1 → Si(111)-7x7 surface phase transformation. [27] The rate of this thermally driven phase transformation was determined by monitoring the disappearance of a SH signal forbidden for the 3m symmetry of the Si(111)-7x7 surface, but allowed for the lower symmetry Si(111)-2x1 reconstruction.

For the clean, reconstructed Si(111) surfaces, it was found [27,28] that the (anisotropic) surface contribution to the SHG process completely dominated that of the bulk. This behavior is to be contrasted with that for the oxidized surfaces, for which the (anisotropic) surface and bulk terms were determined to be of comparable importance. [15,18] The large nonlinearity of these surfaces can be attributed to the presence of strong transitions between well-defined surface states. For the measurements performed with 1.06μm pump radiation, the fundamental and harmonic frequencies lie much more nearly in resonance with transitions between surface electronic states than between the bulk electronic states, which are significant only for energies above the direct bandgap of the material. [27] Recent studies by Tom and Aumiller [29] have examined the nature of the nonlinear response from the clean Si(111)-7x7 surface in considerable detail. A strong variation in certain independent elements of $\chi_S^{(2)}$ with temperature and oxygen exposure have been established. In addition to measurements of the magnitude of different tensor elements of $\chi_S^{(2)}$, relative phases of some of the elements were deduced and indicated the influence of resonant transitions for the 1.06 μm excitation used in the experiment. These data, in conjunction with results obtained from other surface probes, may provide a means of establishing which surface state transitions are important for the isotropic and anisotropic parts of $\chi_S^{(2)}$.

Reactions on Semiconductor Surfaces

The high sensitivity of the SHG process to the atomic structure and symmetry of the surface layer has been utilized in several studies of modifications and reactions on reconstructed semiconductor surfaces. One class of applications involves assessing the degree of surface ordering by means of the strength of the anisotropic terms in the SH response. This simple scheme has been applied to problems in which the chemical composition of the surface is unaltered, but the crystal structure of the surface is disrupted. In this manner, it has been possible to monitor in real time the disordering of Si(111)-7x7 surfaces induced by ion bombardment [28,30] and by deposition of Si on substrates held at room temperature. [31] From these investigations, an average surface area disturbed by each incoming paticle (energetic ion or Si atom) could be inferred. Unlike electron spectroscopies, which also provide monolayer sensitivity, the purely optical SH technique is compatible with environments other than high vacuum. In practical applications, this feature can be quite significant.

For the problem of Si deposition, the SH technique has been demonstrated to be capable of distinguishing epitaxial and non-epitaxial crystal growth with submonolayer sensitivity. [32] To understand some of the fundamental parameters in epitaxial growth, the SH method has been used to monitor the annealing of amorphous Si films of monolayer thickness on Si(111)-7x7 surfaces. [32] Si layers are formed by deposition of atomic Si on the reconstructed Si surface held at room temperature. From the rate of reordering of the amorphous surface layer upon annealing the substrate at various temperatures, the activation energy for the migration of Si adatoms on a Si(111)-7x7 surface has been inferred.

The SH process has also been applied to examine the Si(111)-7x7 surface during the initial stages of oxidation. Both the isotropic [29,33] and anisotropic [28,29] elements of the surface SH response have been recorded. The very high sensitivity of the SH signal to the degree of oxidation, which arises both from the change in the degree of ordering (for the anisotropic terms) and from the large expected perturbation of the surface electronic states, has permitted the real-time studies of oxidation and of thermally induced oxygen desorption to be performed. Analysis of such data can yield important information on the reaction kinetics. In Ref. 33, values for a pre-exponential factor and an activation energy are extracted for the process of oxygen desorption from a Si(111) surface.

The somewhat more complex, but very intriguing system of Au on Si(111) has been probed with the SH technique by McGilp and Yeh.[34] Pronounced changes in the anisotropic response were observed as a function of the amount of metal deposited and the annealing conditions. The authors present evidence that even in the case where a thick metal-silicide layer has been formed, the SH response may be dominated by that of the buried interface. Thus, the SH technique can be easily applied to probe interfaces between two solids, as has previously been seen [1] for other interfaces, such as the liquid-solid interface, between two dense media.

CONCLUDING REMARKS

As this overview has illustrated, considerable progress has been made over the past few years in understanding the nature of the SHG process at the surface of centrosymmetric semiconductors. The sensitivity of the SH response to the electronic properties of the surface is known to manifest itself in a strong dependence of the nonlinear susceptibility on the chemical nature of the surface. This behavior, which is also apparent for surfaces of other solids, [1] has been clearly observed in studies of semiconductor surfaces under controlled conditions. In addition to this effect, however, the investigations of semiconductor surfaces have also brought out the the influence of the detailed atomic structure of the surface on the SHG process. The phenomenological description of SHG in centrosymmetric media that has now been developed can account for the resulting relationship between SH polarization dependence and crystal structure. The challenge of formulating a tractable theory of a more quantitative character, which involves details of the surface electronic structure, still remains.

While the theory of surface SHG continues to advance, numerous applications of the technique to obtain new information about semiconductor surfaces have also emerged. Some of the more unique studies rely on the capability of examining surfaces under reaction conditions and interfaces between semiconductors and other dense media. Another especially promising direction is the use of the time resolution inherent in the SH technique. One example, mentioned above, involves the dynamics of melting. Many other important problems concerning the lifetime of surface excitations may also, it is hoped, be addressed by this technique. A further avenue which has not yet been fully exploited is the possibility of nonlinear spectroscopy. This could take the form either of resonant SHG [12] or of three-wave mixing with two different frequencies. [35] The latter approach retains the surface specific character of the SHG process for centrosymmetric media, but permits the frequency range examined to be conveniently extended into the infrared. As an example of the potential of such studies, resonant SHG and three-wave mixing spectroscopy have recently been applied to examine the electronic structure of the epitaxial insulator/semiconductor interface formed by CaF_2/Si(111). [36] A strong resonant response has been observed for this system, thus permitting a determination of the energy gap between the empty and filled electronic states localized at the interface.

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