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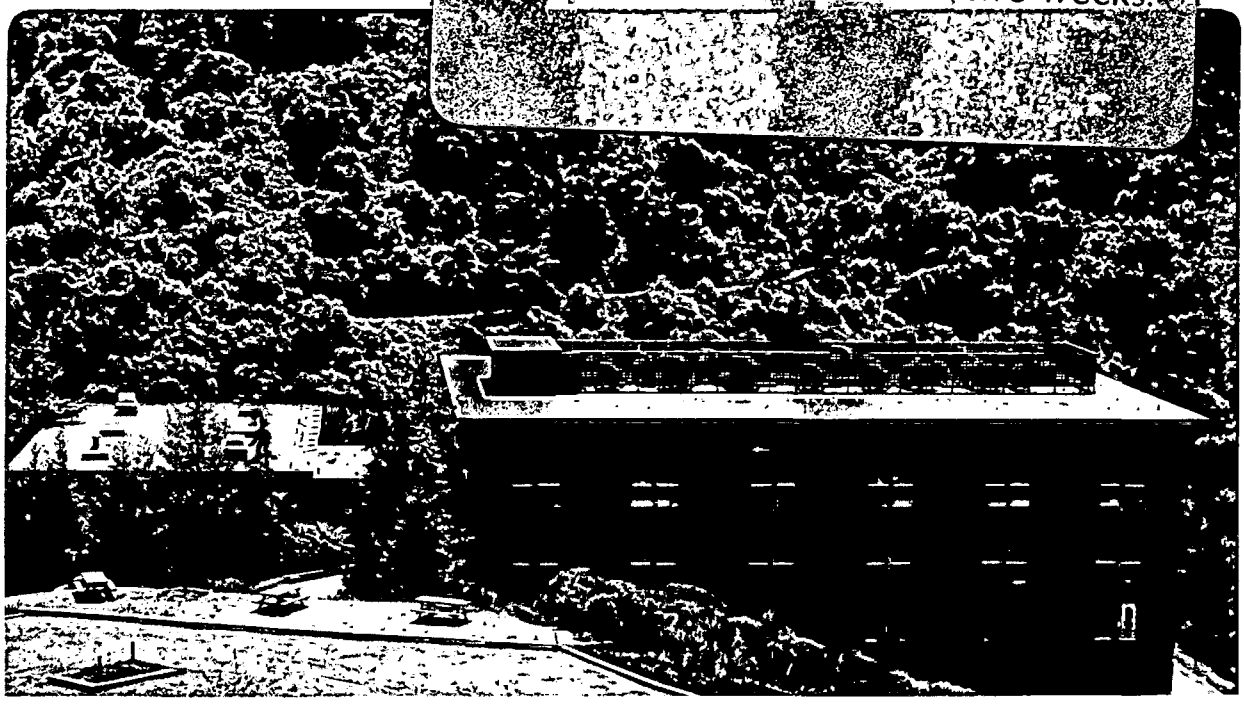

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Abstract

The origins of the surface nonlinearity in surface second harmonic generation are discussed. It is shown that this second-order nonlinear optical process is characterized by a surface nonlinear susceptibility tensor containing both local and nonlocal contributions.

Introduction

Surface second harmonic generation was intensively studied about twenty years ago.[1] Recently, the interest in this area is renewed because of its relevance to surface science. The diversity of the systems encountered in surface studies generally requires the use of a wide variety of techniques. The intrinsic thinness of a surface as well as the necessity to strongly discriminate against a bulk background, however, impose stringent conditions on the development of new techniques. The surface probes most commonly used are massive particles, mainly electrons. Scattering of such particles from a surface allows the deduction of many important properties of the surface. Unfortunately, they are often restricted to an ultrahigh vacuum environment and hence to the studies of vacuum/condensed matter interfaces. Surface probes utilizing optical beams do not have this restriction, and indeed ellipsometric techniques have been used for surface studies in some cases. However, the need for a good discrimination against the signal from the bulk may still limit the usefulness of the technique. In recent years, applications of nonlinear optical processes to surface studies have been attempted. They have the advantages of being optical techniques, but in addition, since the surface nonlinearity is characterized by a tensor of higher dimension than the laser dielectric tensor, more information about the surface ordering or symmetry can be retrieved. The surface nonlinear optical techniques that have been tried out so far are coherent antiStokes Raman spectroscopy (CARS),[2] Raman gain spectroscopy,[3] and second harmonic generation (SHG).[4] The two former ones are third order processes and hence relatively weak, requiring special geometries to enhance the signal strength. Furthermore, the bulk discrimination is not intrinsically better than that with a linear technique. SHG, on the other hand, is one of the lowest order nonlinear optical processes and its detection is relatively easy. In addition, it is intrinsically surface sensitive when a centrosymmetric substrate is used. This property stems from the basic fact that the second-order susceptibility for a centrosymmetric medium is zero in the dipole approximation, but at a surface or interface, the inversion symmetry is necessarily broken.

SHG has already been applied to surface studies of a wide variety of systems,[4] yielding dynamic, spectroscopic, and symmetry information about the surfaces or interfaces. As will be clarified in the following,[5] a SHG experiment measures an effective surface nonlinear susceptibility which is an integrated nonlinear response across the surface. It includes the effects due to spatial variation of the linear dielectric response through nonlocal contributions.

Surface Nonlinear Susceptibility

For our purpose, we will define the interface layer thickness, d, as the region over which the material structure or/and electric field change significantly. The structural change can come from a layer of adsorbates on a surface or from reconstruction of the surface itself, or from any kind of inhomogeneity. The field variation across an interface results from variation of the dielectric constant, and this change happens usually over a few atomic layers. In the first investigations of SHG it was assumed that the field variation was solely responsible for the surface nonlinearity through a quadrupole effect.[1] However, it is clear now that because of the symmetry breaking at the surface, an intrinsic second-order nonlinearity can appear independently of the field across the interface.

By restricting our studies to cases where the interface layer thickness is much smaller than the wavelength, it is then possible to use a perturbation approach[6] to deal with the response of the interface layer to an applied field. Boundary conditions require that the electric field components along the interface ($\hat{x}$ - $\hat{y}$) and the displacement current component along the surface normal ($\hat{z}$) are continuous along the interface layer. The electric field component E_2 along $\hat{z}$, on the other hand, changes rapidly across the layer. The response of this layer to E_2 is therefore expected to be nonlocal. Let the field at frequency ω_1 be $E(\vec{r},\omega_1)$. We can write, in general, the linear and second-order nonlinear polarizations arising from local and nonlocal responses of the medium as:

$$P^{(1)}(\vec{r},\omega_1) = \int \overleftrightarrow{\chi}^{(1)}(\vec{r},\vec{r}',\omega_1)\vec{E}(\vec{r}',\omega_1)d^3r'$$

$$P^{(2)}(\vec{r},2\omega) = \int \overleftrightarrow{\chi}^{(2)}(\vec{r},\vec{r}',\vec{r}'',2\omega)E(\vec{r}',\omega)E(\vec{r}'',\omega)d^3r''d^3r'; \qquad (1)$$

We realize that the macroscopic fields and polarization are obtained from averages of the corresponding microscopic quantities over a macroscopic volume. In the interface layer, both E_3 and $\vec{P}^{(n)}$ can vary rapidly on the atomic scale. Consequently, the definition of a macroscopic quantity is somewhat arbitrary, depending on the averaging volume. However, we know that regardless of the size of the averaging volume, E_2 should change continuously across the interface layer from its macroscopic value in medium 1 to its value in medium 2, and as we shall see later, the surface optical effects generally depend only on the

integrated response of the interface layer to the field, that is, $\int \vec{P}^{(n)}(z)dz$ integrated across the interface layer.

The perturbation approach we use considers a system with a well-defined local dielectric constant on either side of a sharp boundary as the unperturbed system, and the changes in the linear dielectric constant in the interface layer as a small perturbation. We assume a system with translational symmetry in the (x - y) plane such that

$$\vec{E}(\vec{r},\omega) = \vec{\mathscr{E}}(z,\omega)\exp(ik_x x - i\omega t)$$

$$\vec{E}(\vec{r},2\omega) = \vec{\mathscr{E}}(z,2\omega)\exp(i2k_x x - i2\omega t)$$

$$\vec{P}^{(1)}(\vec{r},2\omega) = \vec{\mathscr{P}}^{(1)}(z,2\omega)\exp(i2k_x x - i2\omega t)$$

$$\Delta P^{(1)}(\vec{r},2\omega) = \int \Delta\overleftrightarrow{\chi}^{(1)}(z,z',2\omega)\mathscr{E}(z',2\omega)dz'\exp(i2k_x x - i2\omega t). \quad (2)$$

The solution of linear wave propagation in the unperturbed system is the classical fresnel solution. One can then obtain the Green's function[5] for the equation

$$[\nabla x(\nabla x) - (2\omega/c)^2\overleftrightarrow{\varepsilon}_o]\overleftrightarrow{G} = \overleftrightarrow{\delta}(\vec{r} - \vec{r}'). \quad (3)$$

This Green's function can then be used to solve the wave equation with the linear perturbation and the nonlinear polarization included as source terms

$$\vec{\mathscr{E}}(z,2\omega) = \int \overleftrightarrow{G}(z,z',2\omega)4\pi(2\omega/c)^2[\vec{\mathscr{P}}^{(2)}(z',2\omega) + \int \Delta\overleftrightarrow{\chi}^{(1)}(z',z'',2\omega)\vec{\mathscr{E}}(z'',2\omega)dz'']dz'. \quad (4)$$

From this expression one can see that the perturbation due to the linear term introduces only a correction of the order of d/λ to the radiated field used in ellipsometry and in most cases, can be neglected. The nonlinear polarization exists both in the bulk and at the interface. Because of the possible difference of the susceptibility tensor in the bulk and at the surface and because of the rapid variation of $\mathscr{E}_z$ in the interface layer, which enhances the nonlocal response, $P^{(2)}$ in the surface layer could be significantly different from that in the bulk. In fact, as far as the SHG from centrosymmetric media is concerned, $P^{(2)}$ of the surface layer is typically a factor λ/a larger than $P^{(2)}$ in the bulk, where a is the interatomic distance.

Using some continuity properties of the Green's function,[6] it is possible to express the surface layer contribution to SHG by an effective surface polarization $\vec{P}_s^{(2)}$. The latter is quadratically dependent on the incoming pump field via an effective surface nonlinear susceptibility. To avoid difficulties associated with the ill-defined, rapidly varying $\mathscr{E}_z$ at the interface, we choose to define $\vec{P}_s^{(2)}$ as

$$P_{si}^{(2)}(2\omega) = \chi_{sijk}^{(2)}F_j(0,\omega)F_k(0,\omega)$$

$$F_j(0,\omega) = \mathscr{E}_j(0,\omega) \text{ for } j = x,y$$

$$F_z(0,\omega) = \mathscr{D}_z(0,\omega), \quad (5)$$

where D is the displacement current, the z-component of which is continuous across the interface. If we now write

$$\mathscr{E}_z(z) = s(z,\omega)\mathscr{D}_z(0,\omega), \quad (6)$$

and use Eq. (1) in Eq. (5), we find that in general the effective surface nonlinear tensor can be written as

$$\overleftrightarrow{\chi}_s^{(2)} = \int_{-\infty}^{+\infty}\iint \overleftrightarrow{T}(z)\overleftrightarrow{\chi}^{(2)}(z,z',z'')\overleftrightarrow{S}(z')\overleftrightarrow{S}(z'')dzdz'dz'', \quad (7)$$

where

$$\overleftrightarrow{S}(z) = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & s(z)\end{bmatrix} \quad \text{and} \quad \overleftrightarrow{T}(z) = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1/\varepsilon_o(z)\end{bmatrix}. \quad (8)$$

On both sides of the interface, the system becomes centrosymmetric and the contribution to $\chi_s^{(2)}$ vanishes since

$$\iint \overleftrightarrow{\chi}^{(2)}(z,z',z'')dz'dz'' = 0. \quad (9)$$

The convergence of the integral in Eq. (7) is assured by the fact that s and ε_o become constants away from the interface. In Eq. (7), one can see how dipole and multipole contributions to surface SHG enter. The dipole part coming in through a nonvanishing $\chi^{(2)}$ is the only contribution if the media on two sides of the interface have matching refractive indices. On the other hand, if the dipole part vanishes, then the surface susceptibility arises soley from a nonlocal contribution due to the variation of $\overleftrightarrow{S}$ or $\overleftrightarrow{T}$ when the two media have different dielectric constants. Since the field variation occurs in a few atomic layers, this nonlocal contribution can be of the same order as a possible dipole contribution.

In some cases it is possible to separate experimentally[7] those two contributions by varying the mismatch

of the refractive indices of the media bonding the interface without modifying the surface structure. However, in most cases these two contributions cannot be resolved and the measured quantity is the effective surface susceptibility in Eq. (7), which still contains all the spectroscopic and symmetry features of the interface.

The bulk polarization is more straightforward and was worked out already in 1962-63.[8] For a centrosymmetric medium, the nonlinear polarization is, to the first order, given by electric-quadrupole and magnetic-dipole contributions. Higher-order contributions are negligible since they scale as a/λ times smaller. The simplest centrosymmetric medium has an isotropic symmetry, such as liquids, glasses, and evaporated films. In this case, the nonlinear polarization has the general form

$$P^{(1)}(2\omega) = (\delta - \beta - 2\gamma)(\vec{E} \cdot \vec{\nabla})\vec{E} + \beta\vec{E}(\vec{\nabla} \cdot \vec{E}) + \gamma\nabla(\vec{E} \cdot \vec{E}), \tag{10}$$

where δ, β, and γ are material parameters. This bulk polarization also contributes to the observed signal in surface SHG. Only in the case where the s-polarized SH signal is measured, will this bulk contribution disappear. Fortunately, the surface contribution is at least of the same order, and often much larger, than the bulk contribution. Direct assignment of the origin of the SH signal can be done experimentally by modifying the surface layers.

Conclusion

We have shown in this paper that the surface contribution to second harmonic generation generally comes from both local (dipole) and nonlocal (multipole) effects. This may complicate the applications of SHG, for example, in the measurements of orientation of adsorbates[9] on surfaces, but when an assignment of the origin of the signal can be made, these measurements can still be valid. The nonlocal contribution is also orientation dependent.

Since the surface nonlinearity is characterized by the nonlinear response integrated over the interface layer, it is possible that the most important contribution would be dipole and quadrupole, as integration of higher derivatives gives much smaller contributions. This might simplify the formulation of the surface response.

SHG is, in any case, extremely surface sensitive and a very versatile tool by its applicability to a very wide variety of environments and systems. Further understanding in surface SHG will have to come from a complete microscopic approach to the problem. In this respect, the situation is the same for all the existing surface probes.

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