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1989 J. Phys.: Condens. Matter 1 SB85

(http://iopscience.iop.org/0953-8984/1/SB/015)

J. Phys.: Condens. Matter 1 (1989) SB85–SB92. Printed in the UK

Optical second-harmonic generation for studying surfaces and interfaces

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Received 23 March 1989

Abstract. Optical second-harmonic generation (SHG) is one of a number of new optical techniques offering monolayer sensitivity. It is shown how the non-linear optical response of a medium can produce a surface-specific second-harmonic signal. The type of information available from SHG studies is outlined. A brief historical review is followed by discussion of recent UHV studies of surface and interface SHG from single-crystal metal and semiconductor systems.

1. Introduction

The use of optical techniques, where photons act as both probe and signal, to study the structure of solids has a long history, but it is only recently that the extraction of surface and interface information has been shown to be possible. The penetration depth of optical radiation, typically 100 nm, militates against surface sensitivity. With optical techniques ('optical' in this work is taken to mean electromagnetic radiation in and around the visible region of the spectrum), special effort is needed to obtain surface information. For example, differential reflectance techniques capable of detecting changes in 1 in 10^5 in reflected intensity have been developed [1], Raman spectroscopy has been applied with particular success to investigating space charge layers at interfaces via the Fröhlich interaction (for a review see [2]), and optical second-harmonic generation (SHG) has been used to probe surface and interface structure by exploiting the symmetry properties of the dielectric susceptibility tensor (for a review see [3]). In view of the increasing activity in this area, together with the special approaches needed, we propose to distinguish such studies from other optical work by using the term 'epioptics' to describe the study of surfaces and interfaces using photons as both probe and signal.

The study of surfaces and interfaces using epioptic techniques offers the following advantages over conventional surface spectroscopies (figure 1): material damage and contamination is largely eliminated; insulators can be studied without the problem of charging effects; buried interfaces are accessible owing to the large penetration depth of the optical radiation.

In this work, we discuss one particular epioptic probe, SHG. The history of SHG is briefly reviewed, followed by an outline of the phenomenological theory and a discussion of recent ultra-high vacuum (UHV) studies. An extensive review of surface SHG has appeared recently, dealing with the literature up to the beginning of 1988 [3].

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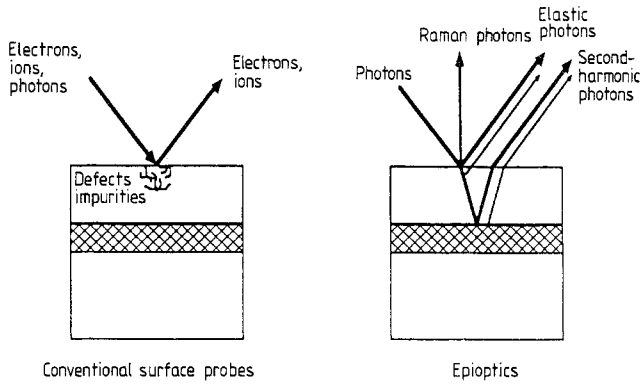

Figure 1. Comparison of conventional and epioptic probes.

2. History

An intense electromagnetic field $\boldsymbol{P}$ will induce a non-linear electric polarisation in a material:

$$\boldsymbol{P} = \varepsilon_0[\chi^{(1)} \cdot \boldsymbol{E}(\omega) + \chi^{(2)} : \boldsymbol{E}(\omega)\boldsymbol{E}(\omega) + \chi^{(3)} : \boldsymbol{E}(\omega)\boldsymbol{E}(\omega)\boldsymbol{E}(\omega) + \ldots]$$

where $\chi^{(i)}$ is the ith-order susceptibility tensor; the second-order term is responsible for SHG. Soon after the detection of bulk SHG it was realised that it might be possible to detect SHG at the surface of centrosymmetric materials [4]. Bulk SHG measured in reflection will be limited to a region about λ from the surface, while the surface contribution is assumed to come from the top atomic layer of dimension a. The surface to bulk SHG intensity will then scale as approximately $(a/\lambda)^2$; in the optical region the surface signal will be about 10^{-6} of the bulk. Now, in the bulk of a solid, the standard multipole expansion of the fields gives contributions to the SHG intensity which scale as $(a/\lambda)^2$. Thus, in the optical region, the electric quadrupole and magnetic dipole terms will contribute about 10^{-6} of the SHG intensity of the electric dipole term. For centrosymmetric solids, such as the metallic and semiconducting elements, the electric dipole contribution is parity forbidden. At the surface of, or interface between, such solids the symmetry is broken, allowing an electric dipole contribution specific to the surface or interface to appear. It follows that, for centrosymmetric solids, the electric dipole surface SHG intensity should be comparable with the bulk electric quadrupole and magnetic dipole SHG intensity and hence be detectable [5, 6].

Initial surface SHG studies in the 1960s under non-UHV conditions detected a surface signal but found no dependence on adsorbate or surface structure [4], and this undoubtedly held back the development of the field. It was mainly the work of Shen's group in Berkeley in the early 1980s which established the potential of SHG as a surface probe (for a review see [7]). Figure 2 shows SHG from Si(111) and Si(100) wafers, in air, as a function of azimuth, for fixed probe and signal polarisations [8]; the dependence of the SHG signal on surface crystallography is clearly revealed. The first UHV study, where conventional surface probes were used to characterise the surface, appeared in 1984. The adsorption of O and CO damped the SHG signal from Rh(111), while the adsorption of Na enhanced it [9]. The following year the azimuthal dependence of the SHG signal was shown to be sensitive to the symmetry change between the (2×1) and (7×7) reconstructions of the Si(111) surface [10] (figure 3). The Au–Si(111) system was used to

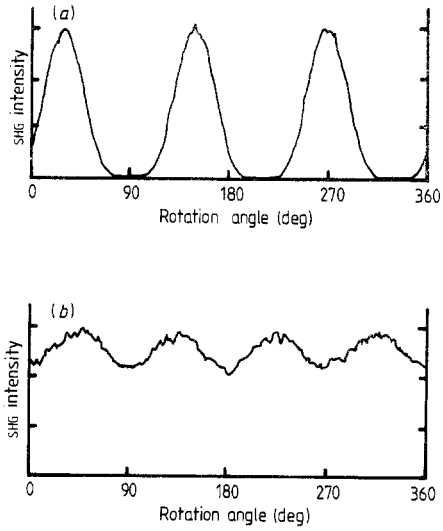

Figure 2. Intensity (in arbitrary units) of p-polarised SHG reflection from (*a*) Si(111) and (*b*) Si(100) faces under p-polarised excitation, as a function of azimuthal angle (after [8]).

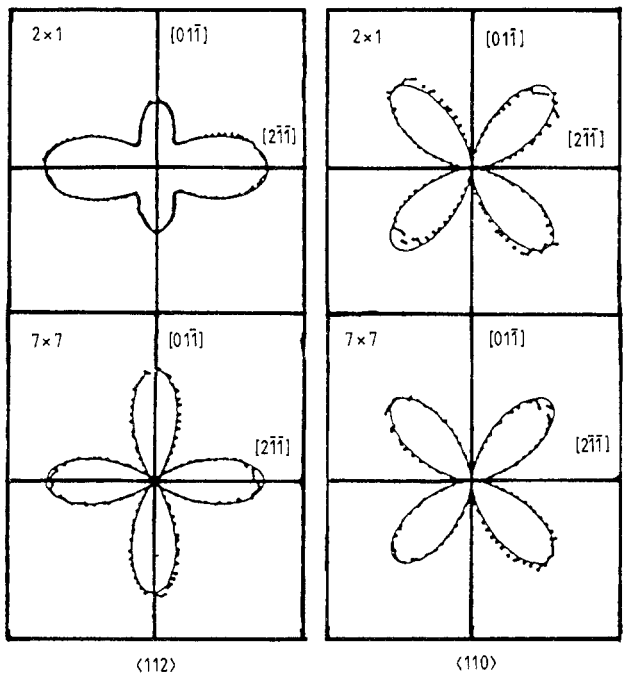

Figure 3. SHG intensity, polarised along the ⟨112⟩ and ⟨110⟩ azimuths, from Si(111)2 × 1 and Si(111)7 × 7 surfaces, as a function of the polarisation of the normally incident pump beam (after [10]).

show that SHG could provide structural information about buried metal–semiconductor interfaces [11, 12]. SHG from the surface of GaAs has also recently been observed [13, 14], thus extending the technique to non-centrosymmetric solids. Less structural information is directly available from these solids because some of the surface susceptibility tensor components cannot be separated from the bulk components.

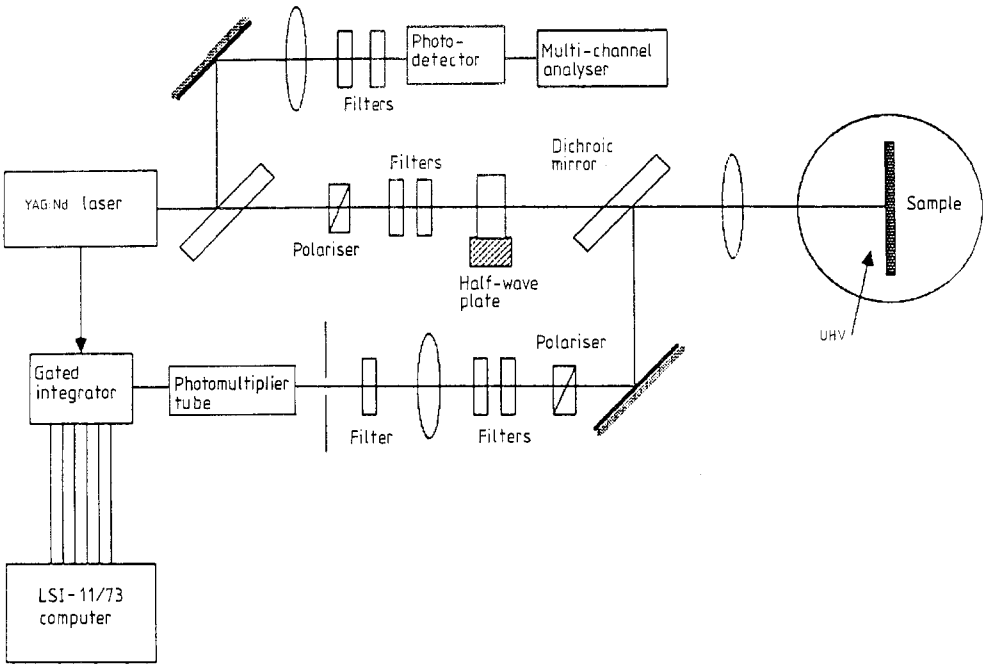

Figure 4. Typical apparatus for studying SHG at surfaces and interfaces (after [12]).

3. Phenomenological theory

The standard approach uses an induced dipole sheet on a uniform medium as the surface SHG source and finds an expression for the second-harmonic polarisation $P(2\omega)$, either by applying boundary conditions to the sheet [15], or by a more general Green function approach [16]:

$$P(2\omega) \propto |\boldsymbol{e}^{2\omega} \cdot \chi^{s} : \boldsymbol{e}^{\omega}\boldsymbol{e}^{\omega}|^2 P^2(\omega)$$

where χ^s is the surface non-linear susceptibility tensor, and $\boldsymbol{e}^{\omega}$ and $\boldsymbol{e}^{2\omega}$ are the effective polarisation vectors. χ^s transforms with the point group symmetry of the surface, allowing structural information to be deduced by appropriate choice of experimental geometry and polarisation vectors. Of particular interest is the use of normal incidence to produce simplified expressions [10–12]. For a solid with a surface or interface in the x–y plane, and normally incident radiation linearly polarised at an angle θ to the x axis, the SHG intensity is given by [12]

$$I_x(2\omega) \propto |\chi^{s}_{xxx} \cos^2\theta + \chi^{s}_{xyy} \sin^2\theta + \chi^{s}_{xyx} \sin(2\theta)|^2$$
$$I_y(2\omega) \propto |\chi^{s}_{yxx} \cos^2\theta + \chi^{s}_{yyy} \sin^2\theta + \chi^{s}_{yxy} \sin(2\theta)|^2.$$

The presence of symmetry elements in the surface produces further simplification; for example, for a single mirror plane in the surface the components $xyx = yyy = yxx = 0$. Figure 4 shows the type of experimental configuration used, while figure 5 shows the polarisation plots obtained, as a function of θ, for Au adsorbed on Si(111); the full curves are least-squares fits to the above equations. The change in pattern as a function of Au coverage at room temperature provides information about structural changes at the buried Au–Si(111) interface [12].

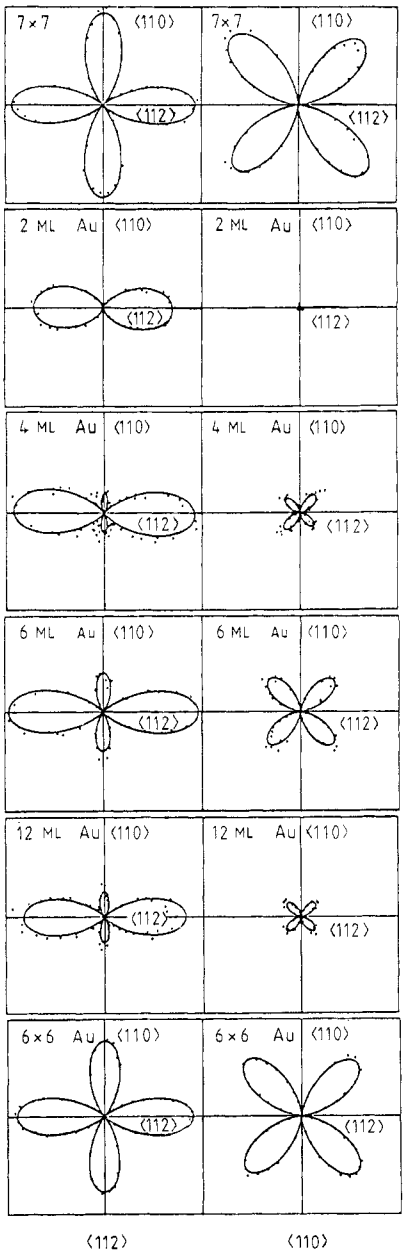

Figure 5. SHG intensity, polarised along the ⟨112⟩ and ⟨110⟩ azimuths, from Si(111)7 × 7 and Si(111)–Au (after [12]).

4. Recent results

The last two years have seen a substantial increase in the number of UHV-based SHG studies. Three recent studies serve to illustrate the potential of SHG [17–19].

Dynamical screening at a metal surface has been directly probed by SHG [17]. Figure 6(*a*) shows the variation in SHG intensity as a function of the thickness of a Rb film on a Ag(110) surface. Such short-wavelength oscillations are unexpected from a probe using optical wavelengths and are attributed to Friedel-type screening oscillations extending

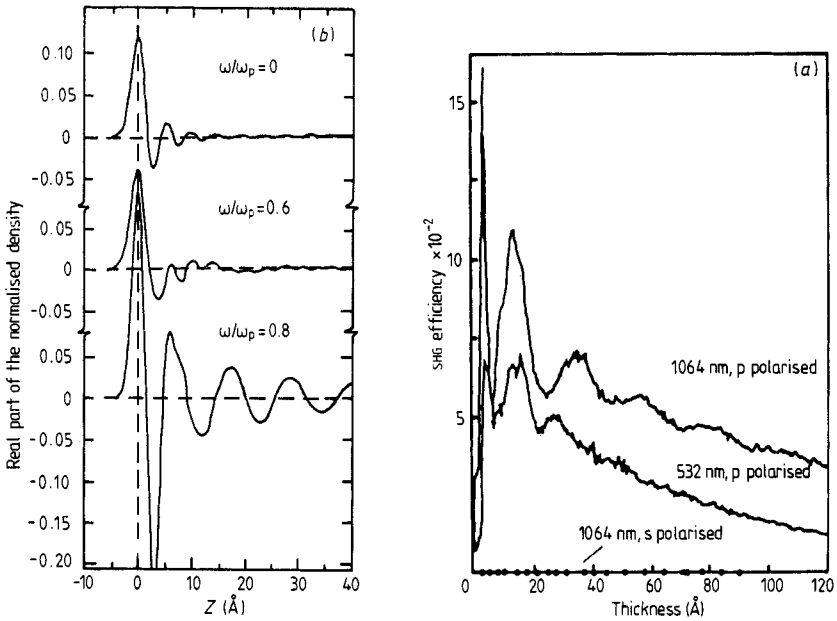

Figure 6. (*a*) SHG intensity as a function of Rb film thickness for two different wavelengths of p-polarised light (Rb/Ag(110), 60°). (*b*) Real part of the normalised density induced at a metal surface by a uniform electric field normal to the surface, for a screening radius r_s of 5 au (after [17]).

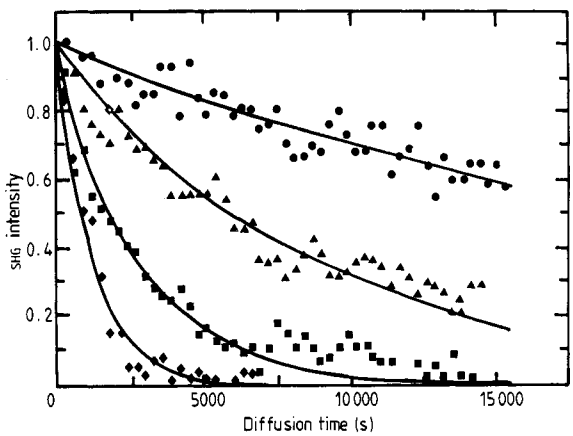

Figure 7. Normalised first-order diffracted SHG intensity (in arbitrary units) as a function of time at various sample temperatures after laser desorption (after [18]): ●, 219 K; ▲, 247 K; ■, 261 K; ◆, 273 K; —— fits to a one-dimensional diffusion equation.

from the surface into the metal. Figure 6(*b*) shows the normalised electron density from a jellium calculation, as a function of depth and excitation frequency. This direct imaging of the longitudinal screening field (note the lack of s-polarised signal in figure 6(*a*)) occurs because the oscillatory SHG intensity originates from the product of the longitudinal and transverse field strengths at the interface. We note that the initial increase in the SHG intensity of a factor of 1600 at 1064 nm excitation wavelength, and of a factor of only 10 at 532 nm, remains unexplained [17].

In our second illustration, SHG was used to measure the surface diffusion of CO on Ni(111) [18] (figure 7). In this elegant experiment the interference of two 1064 nm laser

beams was used to prepare a monolayer grating of CO by desorption. A third beam of 532 nm was used for the SHG measurements. The specular SHG beam monitored the average CO average, while the time dependence of the first-order diffracted SHG beam provided a measure of the diffusion rate of the CO molecules, diffusion wiping out the diffraction grating with time. The activation energy for diffusion obtained agreed well with the values obtained by other methods. This technique appears to be particularly suited to measuring the dependence of diffusion on crystal azimuth [18].

Finally, resonant SHG and sum-frequency generation (another three-wave mixing technique) has been applied to the CaF_2–Si(111) interface [19]. The importance of resonance effects, involving surface and interface states, in the full exploitation of surface and interface SHG has been clear for some time [12], and this work [19] is the first example of the use of resonant three-wave mixing to determine an interface-state band gap. A value of 2.4 eV is found, together with some evidence for a bound two-dimensional exciton 150 meV below the interface band edge.

5. Conclusion

In this brief review we have attempted to show the potential of SHG as a new surface and interface probe. It is clear that, for centrosymmetric material, SHG can provide structural information about surfaces and buried interfaces. Non-centrosymmetric material, such as GaAs, can also be studied, but less information is directly available because only some surface tensor components are separable from the bulk contribution [13]. The effect of surface and interface electronic structure on the SHG signal is beginning to be investigated via resonance effects observed with tunable sources [19]. Much interesting physics remain to be understood.

Acknowledgments

We thank Dr F J Himpsel for communicating results prior to publication. The term 'epioptic' was coined during discussions about an EC ESPRIT project, involving the Universities of Dublin, Messina, Liverpool, Cardiff and Roma II Tor Vergata, the Technical University of Berlin and the Royal Signals and Radar Establishment, Malvern.

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