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1991 J. Phys.: Condens. Matter 3 S193

(http://iopscience.iop.org/0953-8984/3/S/031)

J. Phys.: Condens. Matter 3 (1991) S193–S198. Printed in the UK

Characterization of the Si(111)–Ga interface using optical second-harmonic generation

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Received 25 April 1991

Abstract. Ultra-high-vacuum studies of optical second-harmonic generation (SHG) from well-characterized Si(111)–Ga interfaces in the submonolayer coverage régime are reported. Both intensity and phase measurements of the SH signal have been made. The χ_{xxx} and χ_{zxx} susceptibility tensor components are shown to have resonant enhancement around a third of a monolayer, for 1064 nm excitation. The origin of this behaviour is discussed in terms of the structure and bonding at the interface.

1. Introduction

Optical second-harmonic generation (SHG) is attracting much interest as a sensitive surface and interface probe [1–3]. Studies of model systems are currently being used to elucidate the relation between the non-linear optical response and the interfacial electronic structure. In this paper SHG from the Si(111)–Ga system in the submonolayer region is reported.

2. Theory

SHG arises from the non-linear polarization $\boldsymbol{P}(2\omega)$ induced by an incident laser field $\boldsymbol{E}(\omega)$:

$$P_i(2\omega) = \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega) \tag{1}$$

where the second-order susceptibility tensor $\chi^{(2)}$ contains material parameters. For a centrosymmetric medium, $\chi^{(2)}$ is non-vanishing only at symmetry breaking interfaces, giving rise to the surface sensitivity of SHG. Due to the large field gradients normal to the surface, higher order (quadrupole) bulk terms can show up as effective surface contributions [4]. The phenomenological treatment of the surface SH response is well known and allows symmetry arguments to be used in the interpretation of experimental data [5–7]. Expressions for the total second-harmonic fields from the (001), (110)

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0953-8984/91/SAS193+06$03.50

and (111) faces of cubic centrosymmetric crystals have been tabulated [7]. Appropriate choice of experimental geometry and polarization vectors then allows structural information to be deduced. For a crystalline surface of $3m$ symmetry excited by a single n-polarized pump beam at frequency ω, the total SH fields are given by

$$E_{ss}(2\omega) = cf_1\chi_{xxx}\sin(3\varphi)E_s(\omega)^2 \tag{2}$$

$$E_{sp}(2\omega) = cf_2\chi_{xxx}\sin(3\varphi)E_p(\omega)^2 \tag{3}$$

$$E_{ps}(2\omega) = c[f_3\chi_{zxx} + f_4\chi_{xxx}\cos(3\varphi)]E_s(\omega)^2 \tag{4}$$

where $E_{m,n}$ indicates the m-polarized SH response for a n-polarized pump beam, c is a constant, the f_i are Fresnel factors, φ is the angle between the x-axis (parallel to $\langle 112\rangle$) and the plane of incidence, and z is along the surface normal. In general, the susceptibility components are complex: $\chi_{ijk} = |\chi_{ijk}|e^{i\phi}$ where ϕ is the phase. In the absence of resonances $\phi = 0°$ or $180°$. Equations (2)–(4) show the sensitivity of SHG to surface symmetry [8]. For $\varphi = 30°$, χ_{xxx} and χ_{zxx} can be measured independently, which is particularly useful for coverage-dependent studies.

3. Experiment procedure

The experiment was carried out in a UHV chamber equipped with conventional diagnostics. Gallium was evaporated from a Knudsen cell onto the clean Si(111)7 × 7 surface, as determined by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The system base pressure was better than 8×10^{-9} Pa, and the pressure remained below 10^{-7} Pa during deposition onto the substrate, which was held at 850 K. The sample was allowed to cool prior to SHG measurements. The flux from the Knudsen cell was calibrated using a quartz crystal monitor, and the Si(111)$\sqrt{3} \times \sqrt{3}$-Ga LEED pattern was observed to be best developed at one-third-monolayer coverage, as was expected from previous work [9].

A Q-switched Nd/YAG laser was used for the SHG experiments at 1064 nm, incident at 67.5° to the sample normal. The pulse length was 15 nsec at 20 Hz repetition rate. A dye laser, pumped by the frequency-doubled output of the Nd/YAG laser, was used for excitation at 634 nm. Laser pulse energy was maintained below 1 kJ m^{-2} to avoid any laser-induced desorption or damage effects. The SH intensity is typically a few photons per pulse at these energy levels and can be calibrated by inserting an x-cut quartz plate in the input beam and observing the Maker fringes [10] produced by SHG in the bulk of the quartz. This calibration technique [11] has the advantage that the experimental geometry, and hence system sensitivity, remains unchanged. χ_{xxx} for quartz at 1064 nm excitation is $6.4(8) \times 10^{-13}$ m/V, where the error in the last figure is given in parenthesis [12]. Dispersion is neglected as all excitations in this study are well within the quartz band gap.

The phase of the SH signal was measured by inserting a quartz plate in the output line and traversing it along the beam, while monitoring the combined SH intensity from the sample and the quartz. The dispersion in air of the fundamental and SH signals produces a variation in the optical path length of the two SH signals, allowing their phase difference to be measured [11].

4. Results and discussion

As SHG from clean Si(111) surfaces using 1064 nm excitation is known to have negligible contribution from bulk higher order terms [2], and the SH intensity from the Si(111)–Ga system (figures 1 and 2) is comparable to, or bigger than, the clean surface and interface, it follows that the SH signal originates at the surface and interface.

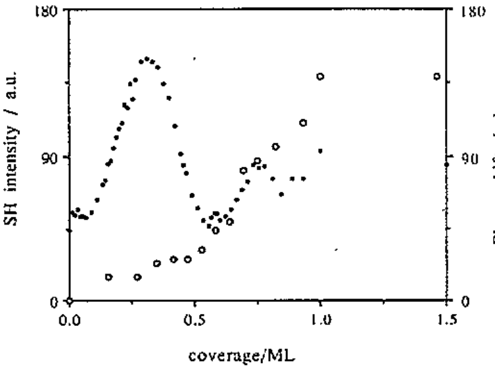

Figure 1. SH intensity (●) for p-polarized input and s-polarized output and phase shift (○) for s-polarized input and output, as a function of Ga coverage, for 1064 nm excitation.

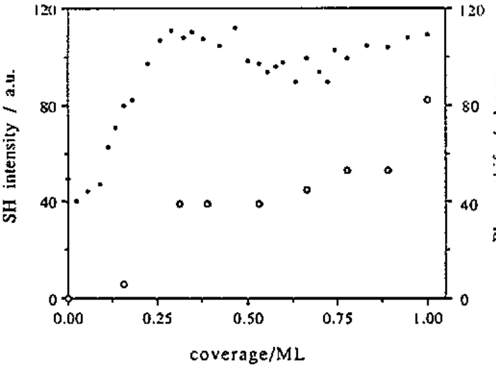

Figure 2. SH intensity (●) and phase shift (○) for s-polarized input and p-polarized output, as a function of Ga coverage, for 1064 nm excitation.

For 1064 nm excitation, figure 1 shows the intensity variation, $I_{sp}(2\omega)$, and the phase shift of $I_{ss}(2\omega)$, as a function of coverage. Equations (2) and (3) show that these data probe the response of χ_{xxx}. Figure 2 shows corresponding data probing χ_{zxx}. The variation in phase shows that the response is close to an electronic resonance at either ω or 2ω. In previous work the work function change on Ga adsorption on Si(111)7 × 7 has been measured to be only 0.1 eV [9] which makes a significant work-function contribution to the variation of SH intensity with coverage unlikely [13].

A simple linear model can be used as a first approach to analysing the coverage dependence of these SHG signals. An analogous model has been applied to SHG from the Si(001)–Ba system by Hollering *et al* [14]. The total response of the system, as a function of Ga coverage, θ, can be written as:

$$|\chi|\mathrm{e}^{\mathrm{i}\phi} = (1-\theta)|\chi_{\mathrm{Si}}|\mathrm{e}^{\mathrm{i}\phi(\mathrm{Si})} + \theta|\chi_{\mathrm{Ga}}|\mathrm{e}^{\mathrm{i}\phi(\mathrm{Ga})} \tag{5}$$

where Ga refers to the Si–Ga interface contribution. The experiments measure $|\chi|^2$ and the relative phase, $[\phi(\mathrm{Ga}) - \phi(\mathrm{Si})]$. Some algebraic manipulation allows $|\chi_{\mathrm{Ga}}|$ to be expressed in terms of these measured quantities. Results are shown in figures 3 and 4. It is interesting to see that both components now reveal a peak around the one-third-monolayer region, strongly suggesting absorptive behaviour. At this coverage the Si(111)$\sqrt{3} \times \sqrt{3}$–Ga structure was seen by LEED in accordance with earlier work [9]. The electronic structure of this system, determined by angle-resolved photoemission and inverse photoemission [15], reveals suitable levels separated by 2.3 eV, the energy of the SH photon for 1064 nm excitation.

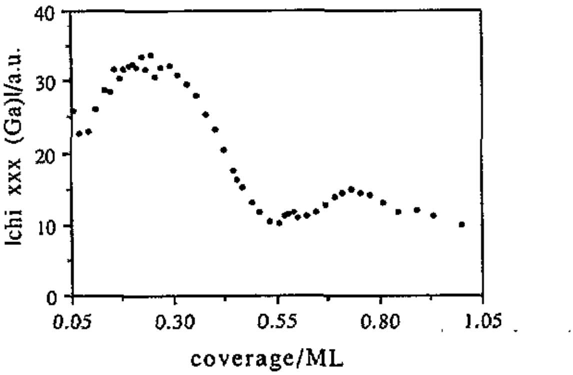

Figure 3. $|\chi_{xxx}(\mathrm{Ga})|$ as a function of coverage, for 1064 nm excitation.

While these phase measurements reveal the presence of an electronic resonance, to do real spectroscopy with SHG the excitation frequency should be varied. Preliminary results using 634 nm excitation show completely different behaviour. No phase shift is observed and SH intensity increases monatonically in the submonolayer régime. Previous work has shown that SHG from Si(111)7 × 7 is enhanced with 1064 nm excitation, but not with 634 nm excitation [16]. These combined results show that there is no absorptive component associated with the Ga adsorbate for 634 nm excitation, but that there is such a resonant enhancement at 1064 nm.

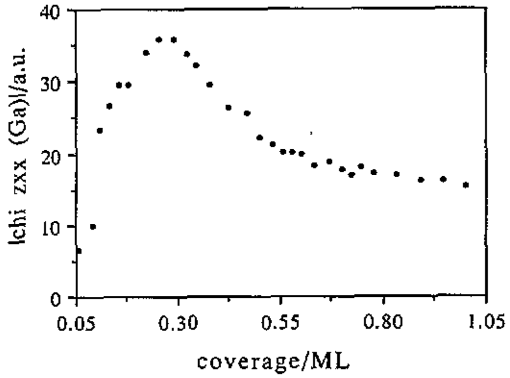

Figure 4. $|\chi_{zxx}(\text{Ga})|$ as a function of coverage, for 1064 nm excitation.

5. Conclusions

SHG from Si(111)–Ga interfaces shows a strong coverage dependence. The combination of intensity and phase measurements allows the identification of a resonant enhancement around one-third monolayer, for 1064 nm excitation. While a complete microscopic model remains to be developed, it is clear from the simple model applied here that SHG has considerable potential in investigating surface and interface structure.

Acknowledgments

This work was supported by EC SCIENCE Twinning Contract SC1-0001-C-(EDB), and by EC ESPRIT Basic Research Action No 3177, 'EPIOPTIC'. Th R would like to thank the group at Trinity College for their hospitality during his stay in Dublin.

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