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Optical second harmonic generation from the Si(111)–Ga interface

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Received 6 May 1991; accepted for publication 8 May 1991

The deposition of Ga on clean Si(111) has a strong effect on the optical second harmonic generation from this surface. By measuring both intensity and phase of the SHG signals, a resonant enhancement is observed around 1/3 of a monolayer for excitation with 1064 nm. This enhancement is absent for 634 nm excitation. These observations are related to the electronic structure of the Si–Ga interface.

1. Introduction

Second-order nonlinear optical techniques like second harmonic generation (SHG) have recently been developed as extremely versatile and sensitive surface and interface probes [1,2]. These so-called "epioptic" [3] probes have some definitive advantages: they are applicable to any interface accessible by light, including those between dense media [4], while their high temporal resolution allows in situ monitoring of surface dynamics [5–7]. For the development and application of SHG for interface studies, a better understanding of the nonlinear sources and the relation between the electronic structure of surfaces and interfaces and their respective nonlinear optical responses is required. For this purpose studies of model systems are particularly useful. The deposition of Ga on Si(111) between 0 and 1 monolayer is studied here using SHG as an in situ probe. By measuring both intensity and phase of the SHG signal, a clear resonant structure near 1/3 of a monolayer is found, for 1064 nm excitation. These results show how SHG can be successfully employed to

study the electronic structure of semiconductor–metal interfaces.

2. Theory

SHG arises from the nonlinear polarization $P(2\omega)$ induced by an incident laser field $E(\omega)$. The surface allowed dipole contribution can be written as:

$$P_i(2\omega) = \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega), \quad (1)$$

where $\chi^{(2)}$ is second-order nonlinear susceptibility tensor reflecting the structure and symmetry properties of the surface layer. In principle, the large field gradients normal to the surface can give rise to higher order bulk nonlinear polarization. However, for clean Si surfaces using 1064 nm excitation, it has been shown experimentally that these bulk contributions are negligible [3]. Expressions for the total second harmonic fields from the (001), (110) and (111) faces of cubic centrosymmetric crystals have been tabulated [8]. Appropriate choice of experimental geometry and polarisation vectors then allows structural information to be deduced.

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For a crystalline surface of 3m symmetry excited by a single n-polarised pump beam at frequency ω , the total SH fields are given by

$$E_{s,n}(2\omega) \sim f_1 \chi_{xxx} \sin(3\varphi) E_s(\omega)^2, \quad (2a)$$

$$E_{p,n}(2\omega) \sim f_2 \chi_{xxx} \sin(3\varphi) E_p(\omega)^2, \quad (2b)$$

$$E_{p,n}(2\omega) \sim [f_3 \chi_{zxx} + f_4 \chi_{xxx} \cos(3\varphi)] E_s(\omega)^2, \quad (2c)$$

where $E_{m,n}$ indicates the m-polarised SH response for a n-polarised pump beam, 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, χ_{xxx} is the anisotropic and χ_{zxx} the isotropic surface contribution. In general, the susceptibility components are complex: $\chi_{ijk} = |\chi_{ijk}| e^{i\phi}$. In the absence of resonances, the phase $\phi = 0^\circ$ or 180° . Eqs. (2) show the sensitivity of SHG to surface symmetry, which has already been applied successfully for the study of surfaces [9], buried interfaces [4,10], melting [5] and steps [11] on Si. In the case of a Si-metal interface, the effective susceptibility can in general be written as:

$$\chi_{\text{eff}} = \chi_{\text{Si}} + \chi_{\text{M}} + \chi_{\text{Si-M}}, \quad (3)$$

where χ_{M} refers to the response of the metal and $\chi_{\text{Si-M}}$ to the Si-M interface. These contributions all depend on the metal coverage and, because this dependence can vary for the different tensor components, the overall response will be complex. However, eq. (2) shows that by choosing $\varphi = 30^\circ$ and a proper combination of input and output polarizations, the χ_{xxx} and χ_{zxx} components can be measured independently, which is particularly useful for coverage dependent studies.

3. Experiment

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 1/3 monolayer coverage, as was expected from previous work [12]. 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 ns 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 [13] produced by SHG in the bulk of the quartz. This calibration technique has the advantage that the experimental geometry, and hence system sensitivity, remains unchanged.

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 [14].

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 [3], and the SH intensity from the Si(111)-Ga system (figs. 1 and 2) is comparable to, or bigger than, the clean surface response, it follows that the SHG signal originates from the surface and interface only.

For 1064 nm excitation, fig. 1 shows the intensity variation $|\chi_{xxx}|^2$ and phase shift as a function of coverage. Fig. 2 shows the corresponding data for χ_{zxx} . The variation in phase indicates that the response is close to an electronic reso-

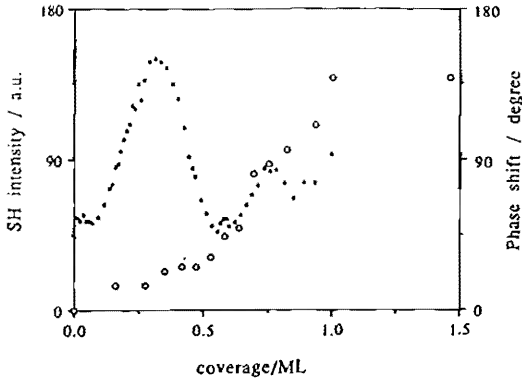


Fig. 1. SH intensity (●) for p-polarised input and s-polarised output and phase shift (○) for s-polarised input and output, as a function of Ga coverage, for 1064 nm excitation.

nance at either ω or 2ω . Previous work has measured the work function change on Ga adsorption on Si(111)7x7 to be only 0.1 eV [12] which makes a significant work function contribution to the variation of SH intensity with coverage unlikely [15].

To analyse the coverage dependence of these SHG signals a simple linear model can be used as a first approximation. The response of the clean Si surface is assumed to decrease linearly with coverage, whereas the Si-Ga response will increase correspondingly. In this simple model there is no metallic Ga component in the submonolayer coverage region. An analogous model has been applied to SHG from the Si(111)-Ba system by

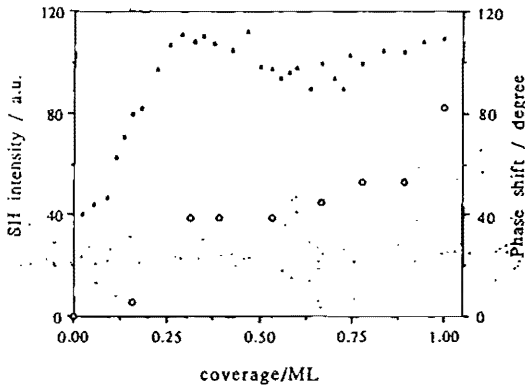


Fig. 2. SH intensity (●) and phase shift (○) for s-polarised input and p-polarised output, as a function of Ga coverage, for 1064 nm excitation.

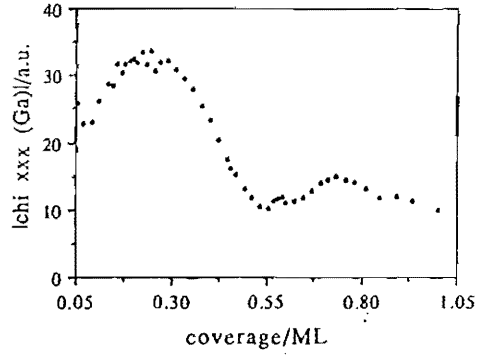


Fig. 3. $|\chi_{xxx}(\text{Ga})|$ as a function of coverage, for 1064 nm excitation.

Hollering et al. [16]. The total response of the system, as a function of Ga coverage, θ , can be written as:

$$|\chi| e^{i\phi} = (1 - \theta) |\chi_{\text{Si}}| e^{i\phi(\text{Si})} + \theta |\chi_{\text{Ga}}| e^{i\phi(\text{Ga})}, \quad (4)$$

where Ga refers to the Si-Ga interface contribution. The experiments measure $|\chi|^2$ and the relative phase, $[\phi(\text{Ga}) - \phi(\text{Si})]$. Some algebraic manipulation allows $|\chi_{\text{Ga}}|$ to be expressed in terms of these measured quantities. Results are shown in figs. 3 and 4. It is interesting to see that both components now clearly reveal a peak around the 1/3 monolayer region, strongly suggesting resonant enhancement. At this coverage the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ga structure was seen by LEED in accordance with earlier work [12]. The electronic structure of this system, determined by angle-re-

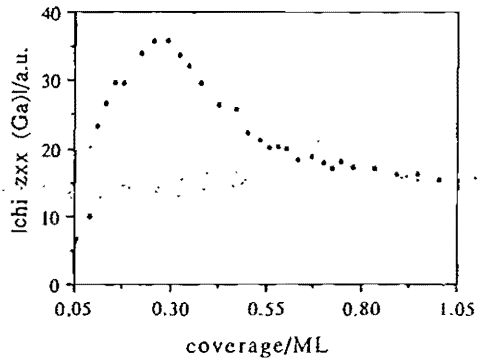


Fig. 4. $|\chi_{zxx}(\text{Ga})|$ as a function of coverage, for 1064 nm excitation.

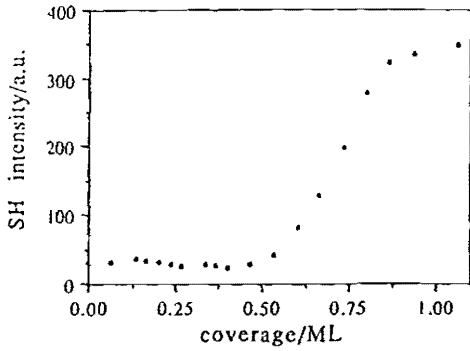


Fig. 5. SH intensity for p-polarised input and s-polarised output, as a function of Ga coverage, for 634 nm excitation.

solved photoemission and inverse photoemission [17], reveals suitable levels separated by 2.3 eV, the energy of the SH photon for 1064 nm excitation, and so it is likely that the enhancement is due to a 2ω resonance.

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 the SH intensity increases monotonically in the submonolayer regime, as shown in fig. 5. Previous work has shown that SHG from Si(111) 7×7 is enhanced with 1064 nm excitation, but not with 634 nm excitation [18]. These combined results show that there is no resonance enhancement associated with the Ga adsorbate for 634 nm excitation, in contrast to the 1064 nm behaviour.

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 1/3 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 electronic structure.

Acknowledgements

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

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