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Study of surface electronic structure of Si(111)–Ga by resonant optical second harmonic generation

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The epitaxial growth of Ga on Si(111) has been studied in situ by optical second harmonic generation (SHG). Enhanced intensity near $\frac{1}{3}$ of a monolayer was observed. By measuring both intensity and absolute phase of the SHG signals, this enhancement can be unambiguously related to electronic resonances of the Si(111)$\sqrt{3} \times \sqrt{3}$–Ga structure.

1. Introduction

The structure of the semiconductor–metal interface is of great fundamental and technological interest, and has therefore stimulated much theoretical and experimental research [1]. Recently, second-order nonlinear optical techniques like second harmonic generation (SHG) have been developed as new and extremely versatile tools for the investigation of the geometrical and electronical structure of surfaces and interfaces [2,3]. These "epioptic" [4] probes have the advantage of being applicable to any interface accessible by light (including those between dense media [5]) and allow nondestructive in situ monitoring of surface dynamics with unprecedented time resolution [6–8].

Preliminary SHG studies of epitaxial Ga deposition on Si(111) showed resonance behaviour around $\frac{1}{3}$ monolayer [9]. However, the origin of this behaviour remained ambiguous. In this paper we will show (to our knowledge for the first time) how absolute phase measurements allow us to ascribe the observed resonance to the Si(111)-$\sqrt{3} \times \sqrt{3}$–Ga structure.

2. Theory

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

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

where $\chi^{(2)}$ is a 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 it has been shown experimentally that these bulk contributions are negligible [4].

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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

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

$$E_{ps}(2\omega) \sim [f_2 \chi_{zxx} + f_3 \chi_{xxx} \cos(3\psi)] E_s(\omega)^2, \quad (2b)$$

$$E_{sp}(2\omega) \sim f_4 \chi_{xxx} \sin(3\psi) E_p(\omega)^2, \quad (2c)$$

where $E_{m,n}$ indicates the m-polarized SH response for an n-polarized pump beam, the f_i are Fresnel factores, ψ 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. Eqs. (2a)–(2c) show the sensitivity of SHG to surface symmetry, which has already been applied succesfully for the study of surfaces [10], buried interfaces [5,11], melting [6] and steps [12] on Si.

In general, the susceptibility components are complex: $\chi_{ijk} = |\chi_{ijk}| e^{i\phi}$. In the absence of resonances $\phi = 0°$ or 180°, while on resonance $\phi = 90°$ or 270°. In the case of a Si–metal interface, the effective susceptibility can in general be written as

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

where χ_M refers to the response of the metal and χ_{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 rather complicated. However, eq. (2) shows that by choosing $\psi = 30°$ and a proper combination of input and output polarizations, the χ_{zxx} and χ_{xxx} components can be measured independently.

3. Experiment

Fig. 1 shows a schematic diagram of the experimental set-up. Gallium was evaporated from a Knudsen cell onto the clean Si(111)7 × 7 surface, as determined by LEED and Auger electron spectroscopy (AES). The system base pressure was better than 10^{-8} 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 meas-

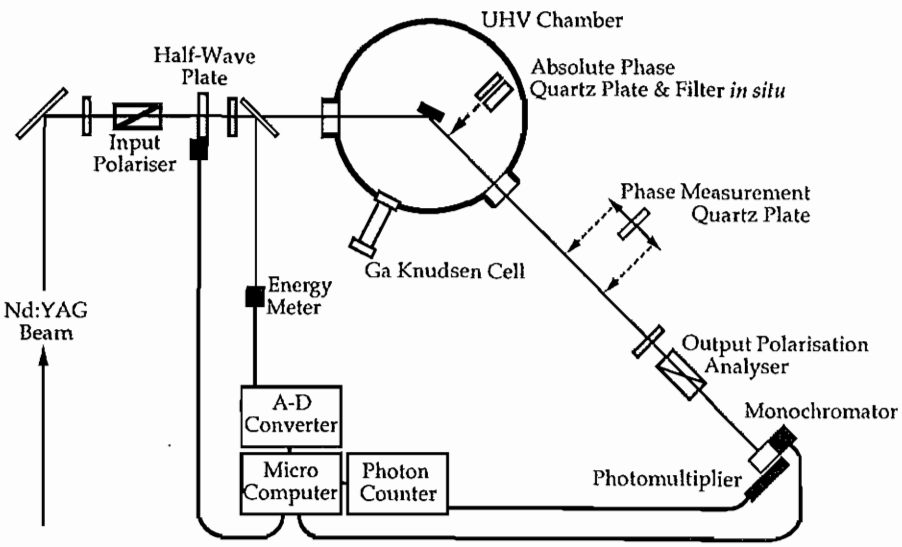

Fig. 1. Experimental set-up for SHG studies under UHV conditions.

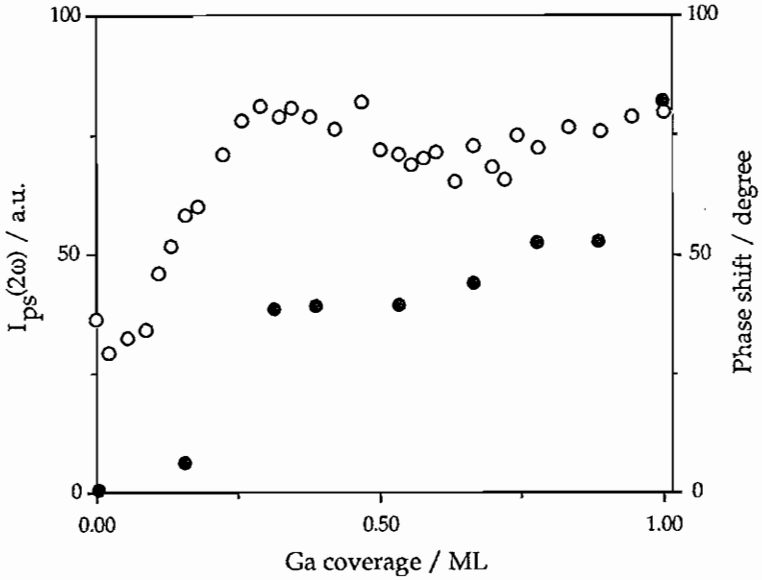

Fig. 2. SH intensity (○) for p-polarized input and s-polarized output and phase shift (●) for s-polarized input and output, as a function of Ga coverage, for 1064 nm excitation.

urements. 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 $\frac{1}{3}$ monolayer coverage, as was expected from previous work [13].

For the SHG experiments a Q-switched

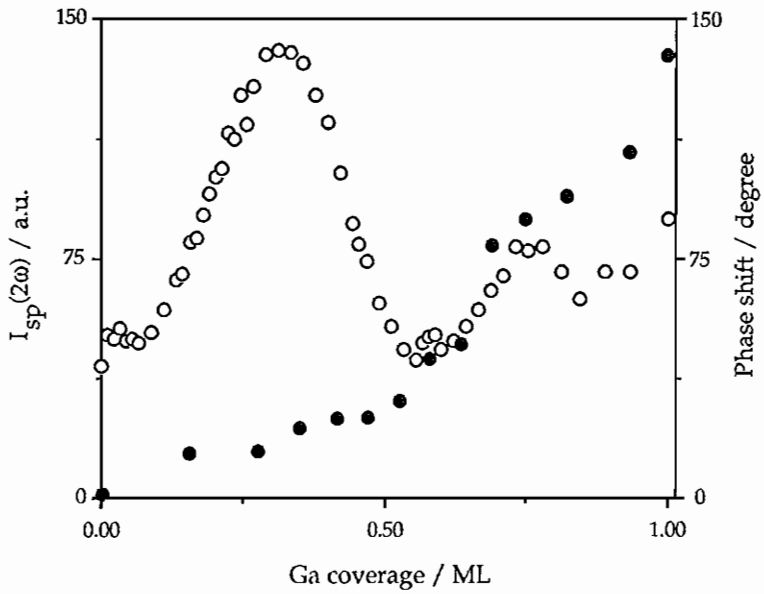

Fig. 3. SH intensity (○) and phase shift (●) for s-polarized input and p-polarized output, as a function of Ga coverage, for 1064 nm excitation.

Nd/YAG laser was used at 1064 nm, incident at 67.5° to the sample normal. The pulse lenght 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 was calibrated by observing the Maker fringes [14] produced by SHG in the bulk of a reference x-cut quartz plate.

The phase change of the SH signal was measured by interfering the sample signal with that of a quartz plate mounted on a translation stage in the output line, making use of the dispersion in air of the fundamental and SH frequencies [15]. In addition, a second quartz plate could be rotated into the output beam, *within* the UHV chamber and without disturbing the optical path. By comparing the phase difference between the two quartz plates, the phase shift arising from the UHV window could be eliminated and the *absolute* phase of the surface signal could be measured. Here, we make use of the fact that, in the frequency range of interest, the quartz reference has an absolute phase angle of zero for χ_{xxx} [16].

4. Results and discussion

For 1064 nm excitation, fig. 2 shows the intensity variation, $I_{sp} \sim |\chi_{xxx}|^2$ and the corresponding phase shift (relative to the Si(111)7 × 7 value) as a function of coverage. Fig. 3 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.

As SHG from clean Si(111) surfaces using 1064 nm excitation is known to have negligible contribution from bulk higher-order terms [4], and the SH intensity from the Si(111)–Ga system (figs. 2 and 3) is comparable to, or bigger than, the clean surface response, it follows that the SHG signal originates from the surface and interface only. The work function change upon Ga adsorption on Si(111)7 × 7 has been measured as only 0.1 eV [13] which makes a significant work function contribution to the variation of SH intensity with coverage unlikely [17,18]. The absolute value of the phase of χ_{xxx} and χ_{zxx} for the Si(111)7 × 7 surface was measured by using the quartz reference in UHV. We found $60 \pm 20°$ for χ_{xxx} and $210 \pm 20°$ for χ_{zxx}. This is the first direct evidence that the SHG response from Si(111)7 × 7 is near resonance for 1064 nm excitation. Note also that the two tensor components are of opposite sign. It has been pointed out previously that there are dangling-bond states at the appropriate energies for resonance [19], and recent linear optical response measurements reveal absorptions around 2 eV also [20].

To analyze the coverage dependence of the SHG signals a simple linear model can be used as a first approximation [9]. This shows a clear resonant peak for both χ components at $\frac{1}{3}$ of a monolayer of Ga. At this coverage, we observed the expected Si(111)$\sqrt{3} \times \sqrt{3}$–Ga LEED pattern [13]. This structure has Ga adatoms in T4 sites [21–23], which saturates the surface and removes all the dangling-bond states [24]. From this it follows that at this coverage the SHG response can only come from the Si–Ga interface, with no Si component. Note that the SHG response cannot come from electronic states associated only with the Ga layer, because that structure has 6-fold symmetry [21–23] for which $\chi_{xxx} \equiv 0$. Therefore, the SHG response must originate from the Si–Ga bonds. Now we can directly determine the phase of the χ_{Si-Ga} components from the data of figs. 2 and 3 and the absolute value for $\phi_{Si(111)}$. In this way we obtain $\phi_{xxx} = (80 \pm 20)°$ and $\phi_{zxx} = (250 \pm 20)°$ for the Si(111)$\sqrt{3} \times \sqrt{3}$–Ga structure. This is direct evidence that the SHG response from this structure is also near resonance. The electronic energy levels of this system, determined by angle-resolved photoemission and inverse photoemission [25], reveals suitable states separated by 2.3 eV, the energy of the SH photon for 1064 nm excitation, and so it is likely that the resonance is at 2ω.

As a further test on this analysis, we have varied the excitation frequency ω. For 634 nm excitation, we have determined the phase shift from the clean Si(111)7 × 7 to be $10 \pm 20°$, i.e. there is no resonant enhancement at this wavelength. Upon Ga deposition, the SHG signal in-

creased monotonically, without any resonance at $\frac{1}{3}$ monolayer and with zero phase shift [9].

At higher coverages the Si(111)–Ga system has been less thoroughly studied. It is thought that the Ga atoms occupy substitutional sites substantially contracted inwards, producing a graphite-like double layer incommensurate with the substrate [23]. There is also some evidence that the sticking probability may fall above $\frac{1}{3}$ monolayer [26], but AES was not sufficiently sensitive to show this effect, under the conditions used in this work. The levelling-off of the SHG response above $\frac{3}{4}$ monolayer may be a sticking probability effect, or it may be showing that more than two surface phases coexist in this coverage region.

Further work is in progress to improve the accuracy of these absolute phase measurements, as they constitute a stringent test of any microscopic model of the SHG response.

5. Conclusions

SHG from Si(111)–Ga interfaces shows a strong coverage dependence. The combination of intensity and phase measurements allows the identification of resonances associated with the Si(111)7×7 and the Si(111)$\sqrt{3}\times\sqrt{3}$–Ga structures, for 1064 nm excitation, and the absence of such resonances for 634 nm excitation. To do more complete spectroscopy with SHG requires the excitation frequency to be varied in the region of resonances, but this is difficult for 1064 nm excitation, which underlines the importance of these phase measurements. While a complete microscopic model remains to be developed, it is clear from the results presented here that SHG has considerable potential in investigating surface and interface electronic structure.

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