

Structure and Ad-Atom Thermal Vibrational Amplitude  
for the Ga/Si(001) 2x1 Surface

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**Abstract**

Fundamental and higher-order harmonic x-ray standing wave measurements were combined to directly measure the lattice positions and thermal vibrational amplitudes of Ga ad-atoms on the Si(001) surface. In this room temperature study, surface structural parameters such as ad-dimer bond lengths were also determined with much higher accuracy than previous studies.

## I. INTRODUCTION

Due to scientific and technological reasons, the structure of group III and V metal's adsorption on the Si(001) surface has long been an interesting subject of surface science.<sup>1-11</sup> The Si(001) clean surface is known to be 2x1 reconstructed by forming dimers to reduce the number of dangling bonds on its bulk truncated surface.<sup>12</sup> The adsorption of group V elements is rather straightforward since they simply break the Si dimers and form an ad-layer of dimers orthogonally oriented with a 1x2 reconstruction.<sup>8-10</sup> However, the adsorption of group III metals on Si(001)2x1 induces different and more complicated surface reconstructions, such as 2x3, 2x5, 2x2 and 1x8.<sup>1,2</sup> Most of these reconstructions occur at coverages less than one half monolayer (ML); where 1 ML =  $6.78 \times 10^{14}$  atoms/cm<sup>2</sup> for Si(001). These surfaces, particularly the Ga/Si(001) surface, have drawn the attention of both experimentalists and theorists.

Experimentally, the Ga/Si(001) surface has previously been studied by reflection high-energy electron-diffraction (RHEED),<sup>1</sup> low-energy electron-diffraction (LEED),<sup>2</sup> Auger electron spectroscopy (AES),<sup>2</sup> scanning-tunneling-microscopy (STM)<sup>3,4</sup> and x-ray standing waves (XSW).<sup>7</sup> Theoretically, a pseudo-potential total energy calculation<sup>6</sup> and a first principles local density molecular cluster (DMol) calculation<sup>7</sup> have been carried out on the Ga/Si(001) system. Prior to our combined study of XSW measurements and DMol calculations,<sup>7</sup> there has been a controversy about the surface structure of low coverage Ga/Si(001) between the orthogonal ad-dimer model<sup>5</sup> and the parallel ad-dimer model.<sup>6</sup> Support of the former is based on studies using measurements, such as RHEED, LEED, AES and STM, while the latter is supported by theoretical pseudo-potential calculations. It was the combined efforts of the high precision XSW measurements and the DMol calculations that clearly ruled out the orthogonal model and confirmed that the Ga atoms form ad-dimers in between Si dimer rows with Ga ad-dimers aligned parallel to the underlying Si dimers as depicted in Fig. 1.

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Although in the previous XSW study we had very precisely measured the Ga ad-dimer height above the bulk-extrapolated (004) plane and achieved an excellent agreement with the theoretical value, our Ga ad-dimer bond length measurements still had a relatively large uncertainty ( $\pm 0.06\text{\AA}$ ). As stated, this was primarily due to a simplified assumption which set the Ga thermal vibration amplitude equivalent to that calculated for Si on a Si clean surface ( $0.12\text{\AA}$ ). As initially demonstrated by Bedzyk and Materlik<sup>13</sup>, the ad-atom's vibrational amplitude can be directly measured by combining the XSW results from a fundamental and higher-order harmonic measurement. For our Ga/Si(001) surface, we will use the (004) and (008) Bragg reflections for this purpose. From these measurements, we will directly determine the Ga thermal vibrational amplitude in the [001] direction on the Si(001) surface at room temperature (RT). As an additional result, we will be able to measure the Ga ad-dimer bond length with greater certainty ( $\pm 0.04\text{\AA}$ ).

## II. XSW TECHNIQUE

The x-ray standing wave technique<sup>14</sup> has proven to be a high-precision probe for solving the structure of ad-atoms on single crystal surfaces.<sup>7,11,13,15-18</sup> The x-ray standing wave is generated by the interference between the incident and Bragg reflected x-ray plane waves and exists both inside the crystal and above its surface. The XSW has a period equal to the corresponding d-spacing of the (hkl) Bragg reflection. When the angle of the crystal (or the incident photon energy) is scanned through the rocking curve of the Bragg reflection from the low angle side to the high angle side, the phase between the reflected and incident plane waves has a  $180^\circ$  shift. This phase shift causes the XSW antinodes (and nodes) to move inward along the (hkl) reciprocal vector  $\mathbf{H}$  by one-half of a d-spacing. The resulting fluorescence yield from ad-atoms has an angular dependence as following:

$$Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)} f_{c,H} \cos[v(\theta) - 2\pi P_H] \quad , \quad (1)$$

where the reflectivity,  $R(\theta)$ , and the phase,  $v(\theta)$ , of the reflected plane wave relative to the incident plane wave are derived from dynamical x-ray diffraction theory. The two parameters that we determine by a  $\chi^2$  fit of Eq. 1 to the data are the coherent position  $P_H$  and the coherent fraction  $f_{c,H}$ . They are the phase and amplitude of the  $H$ th Fourier component of the time-averaged spacial distribution of the ad-atoms projected into a unit cell. Based on the convolution theorem, the coherent fraction can be written as:<sup>13</sup>

$$f_{c,H} = C \cdot a_H \cdot D_H \quad (2)$$

where  $C$  is the ordered fraction,  $a_H$  is the geometrical factor determined by the geometrical structure of ad-atoms, and  $D_H$  is the Debye-Waller factor.

For the case of Ga forming symmetric (non-buckled) ad-dimers on Si(001), Ga ad-atoms have two equally occupied unit cell positions in both the (2x1) and (1x2) Si surface domains. (Fig. 2) In our case, the two domains give identical Ga positions when projected along the [001] or [022] directions. Therefore, we can analyze the problem in terms of one domain (2x1). The coherent position is  $P_{004} = h'/d_{004}$ , where  $h'$  is the height of the Ga ad-atoms above the Si (004) bulk-like lattice plane. Due to thermal vibrations, the time-averaged distribution of Ga is smeared out. If the individual atom has a symmetrical time-averaged distribution about its mean position, the relation between the (008) and (004) coherent position is simply:

$$P_{008} = h'/d_{008} = 2P_{004}. \quad (3)$$

If the Ga ad-dimer is unbuckled (i.e., parallel to the Si(001) surface), the geometrical factors in the [001] direction are unity ( $a_{004} = a_{008} = 1$ ). In the [022] direction the two Ga positions have inequivalent projections, such that the geometrical factor  $a_{022} = |\cos(\pi L/2d_{022})|$ , where  $L$  is the Ga ad-dimer bond length.

The Debye-Waller factor can be expressed in terms of the ad-atom's thermal vibrational amplitude  $\sqrt{\langle u_H^2 \rangle}$  as:

$$D_H = \exp(-2\pi^2 \langle u_H^2 \rangle / d_H^2). \quad (4)$$

Based on Eq. 2 and 4, if the ordered fraction C remains constant during the combined (004) and (008) XSW measurements, we can determine the thermal vibrational amplitude along the [001] direction from the measured (004) and (008) coherent fractions by the following equation:

$$\sqrt{\langle u_{001}^2 \rangle} = \frac{d_{004}}{\sqrt{6}\pi} \sqrt{\ln\left(\frac{f_{004}}{f_{008}}\right)}. \quad (5)$$

### III. EXPERIMENT

The experiments were conducted at the X15A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Our UHV system consists of four coupled chambers allowing sample insertion, preparation (MBE), characterization (LEED and AES), and x-ray measurements. Zegenhagen's review article<sup>18</sup> contains detailed information about the experimental facilities at X15A and the XSW techniques.

The Si(001) sample was first Syton polished and then Shiraki etched<sup>19</sup> to form a thin protective oxide layer. It was then mounted in a strain-free manner on a Mo sample holder and inserted into the UHV chamber. After outgassing at 600°C for 12 hours, the sample was heated to 900°C for 10 minutes to obtain a clean surface by removing the thin oxide layer. After the sample was cooled down to room temperature with an initial cooling rate of 100°C/min, a sharp 2-domain 2x1 LEED pattern was then observed. AES showed that both O and C contamination were below 0.03 ML. With the sample held at room temperature, Ga was then evaporated from

a Knudsen cell held at 830°C. This produced a Ga flux of approximately 0.25 ML/min at the sample surface. The sample was exposed to the Ga effusion for 90 seconds. The Ga coverage was found to be 0.3 ML by using a previously determined calibration for the Auger ratio of the Ga and Si peaks. The LEED pattern was 2x2 after the Ga deposition. The sample was then transferred into the x-ray chamber where XSW measurements were undertaken.

The double crystal monochromator at X15A produces a monochromated and collimated incident x-ray which is directed into the UHV chamber through a Be window for a non-dispersive reflection from the sample. The sample was held at room temperature by a UHV sample manipulator. (Fig. 3) We performed XSW measurements using the Si (004), (008) and (022) reflections. For each measurement, the incident photon energy was tuned to 12.0 keV, which is above the Ga K absorption edge. During the (008) measurement, a 150- $\mu\text{m}$  Al foil was placed in front of the monochromator to attenuate the coexisting 6.0 keV photons from the (004) reflection to 1%. While the incident photon energy was scanned (equivalent to scanning the sample in angle) through the rocking curve, we simultaneously collected both the reflected x-ray intensity from a Si photo diode inside the UHV chamber and the x-ray fluorescence spectra from an energy dispersive Si(Li) detector. Fig. 4(a) and (b) illustrate experimental data for the Si reflectivity and Ga  $K\alpha$  fluorescence yield as well as best fits to the dynamical diffraction theory (Eq. 1) for the Si (004) and (008) reflections, respectively. Coherent fractions and coherent positions determined from (004), (008) and (022) measurements are listed in Table 1.

#### IV. RESULTS AND DISCUSSIONS

The measured (004) coherent position is  $P_{004} = 0.77 \pm 0.01$ . Therefore, the height of the Ga ad-dimer above the Si(004) bulk-extrapolated lattice plane  $h' = P_{004} \cdot d_{004} = 1.04 \pm 0.01 \text{ \AA}$ . This measurement is consistent with our previous XSW measurements and the DMol calculation predicted value for  $h'$ .<sup>7</sup>



As shown before, the Debye-Waller factor can be determined by Eq. 5, if the ordered fraction  $C$  is constant. To assure this, we performed the (004) XSW measurement on the same surface before and after the (008) measurement. We were able to obtain exactly the same  $f_{004}$  and  $P_{004}$  values within the range of error for both (004) scans. This indicates that the surface structure and the ordering are very stable over a long period of time (20-30 hours) required by the combined (004) and (008) measurements. Using Eq. 5, we found that the [001] thermal vibrational amplitude of the Ga ad-atom on the Si(001) surface at room temperature is  $0.135 \pm 0.01 \text{ \AA}$ . The corresponding Ga ordered fraction was  $C = 0.74$  for this surface preparation.

Prior to this work, temperature dependencies of the coherent fraction ( $\propto D_H$ ) of Ga/Si(111)<sup>16</sup> and As/Si(001)<sup>11</sup> have been measured by XSW methods, which did not employ higher-order harmonic reflections. These were indirect measurements of  $\sqrt{\langle u_H^2 \rangle}$  since they did not obtain the absolute value of  $\sqrt{\langle u_H^2 \rangle}$  of the ad-atom on the Si surface. Instead, the value at RT was assumed to be the same as that calculated for the Si clean surface at RT. In the initial higher-order harmonic thermal vibrational amplitude XSW measurement the Br/Ge(111) was studied in an inert gas environment rather than UHV. As a result, the Br coverage and ordered fraction were not as well regulated as our present study. This resulted in a much larger uncertainty in the ad-atom's vibrational amplitude.

For comparison, Table 2 lists measured and calculated values of  $\sqrt{\langle u_H^2 \rangle}$  for clean and Ga adsorbed Si surfaces. Our measured value of the Ga thermal vibrational amplitude is 12% larger than the calculated value of the Si(001) clean surface and 25% larger than that of the Si(111) clean surface. In general, one should expect a difference, since Ga has a different chemical bonding configuration with the Si surface.

To determine the Ga ad-dimer bond length  $L$ , the geometrical factor  $a_{022}$  has to be determined from the (022) measurement using Eq. 2. Both experiment<sup>11</sup> and calculation<sup>20</sup> have shown that the anisotropy of the thermal vibration amplitude on Si(001) is rather small at room temperature. Lacking a (044) XSW measurement we will assume that the Ga ad-atom has the same thermal vibration amplitude along both [001] and [022] directions. Therefore, the Debye-

Waller factor  $D_{022} = 0.91$ . And the ordered fraction is 74% as shown above. Thus, the Ga ad-dimer bond length  $L$  is determined to be  $2.58 \pm 0.04 \text{ \AA}$ . The DMol calculation predicted value  $L = 2.65 \pm 0.05 \text{ \AA}$ <sup>7</sup> and the pseudo-potential calculation predicted  $L$  to be  $2.63 \text{ \AA}$ <sup>6</sup> are in good agreement with our measurement.

Ideally, the (008) coherent position should be twice the (004) coherent position (use modulo 1). Our measured value  $P_{008} = 0.58 \pm 0.02$  is slightly (0.04) larger than that predicted from the (004) value. The (008) determined  $h'$  value is  $0.03 \text{ \AA}$  higher than the (004) value. Although this difference may not be appreciable for most structural techniques, it is not within the XSW uncertainty range (typically,  $\pm 0.01 \text{ \AA}$ ). From the present data, we do not have sufficient information to fully interpret this reproducible feature in our measurement. The most probable cause is an asymmetry in the bonding potential which causes the Ga ad-atom time-averaged spatial distribution to be asymmetrical in the [001] direction. In future temperature dependent studies, we will more thoroughly explore the sensitivity of the higher-order harmonic coherent position to this anharmonicity effect.

## V. CONCLUSIONS

We have measured the position and thermal vibrational amplitude of Ga ad-atoms on the Si(001) surface at room temperature using the Si (004), (008) and (022) XSW measurements. Our higher-order harmonic XSW measurements directly determine the [001] Ga thermal vibrational amplitude on the Si(001) surface at room temperature to be  $0.135 \pm 0.01 \text{ \AA}$ , which is more than 10% larger than the calculated value for the Si clean surface. The Ga ad-dimer is found to be  $1.04 \pm 0.01 \text{ \AA}$  above the Si(004) bulk extrapolated lattice plane and the Ga ad-dimer bond length is found to be  $2.58 \pm 0.04 \text{ \AA}$ . These values agree very well with the previous theoretically predicted values for the parallel ad-dimer model in which the Ga ad-dimer is parallel to the underlying Si dimer.

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TABLE 1. Structural parameters determined by (004), (008) and (022) XSW measurements for the Ga/Si(001) 2x2 surface.

	coherent fraction	Coherent position
(004)	$0.61 \pm 0.01$	$0.77 \pm 0.01$
(008)	$0.34 \pm 0.02$	$0.58 \pm 0.01$
(022)	$0.35 \pm 0.01$	$0.91 \pm 0.01$

TABLE 2. Measured and calculated thermal vibration amplitudes  $\sqrt{\langle u_H^2 \rangle}$  at room temperature.

	Bulk Si <sup>a</sup>	Si on Si(111) <sup>b</sup>	Si on Si(001) <sup>c</sup>	Ga on Si(001)
$\sqrt{\langle u_H^2 \rangle}$ (Å)	0.075	0.120	0.107	0.135

a Ref. 21

b Ref. 22

c Ref. 22

Figure Captions:

**FIG. 1.** Three-dimensional structural model of the Ga/Si(001) 2x2 surface.

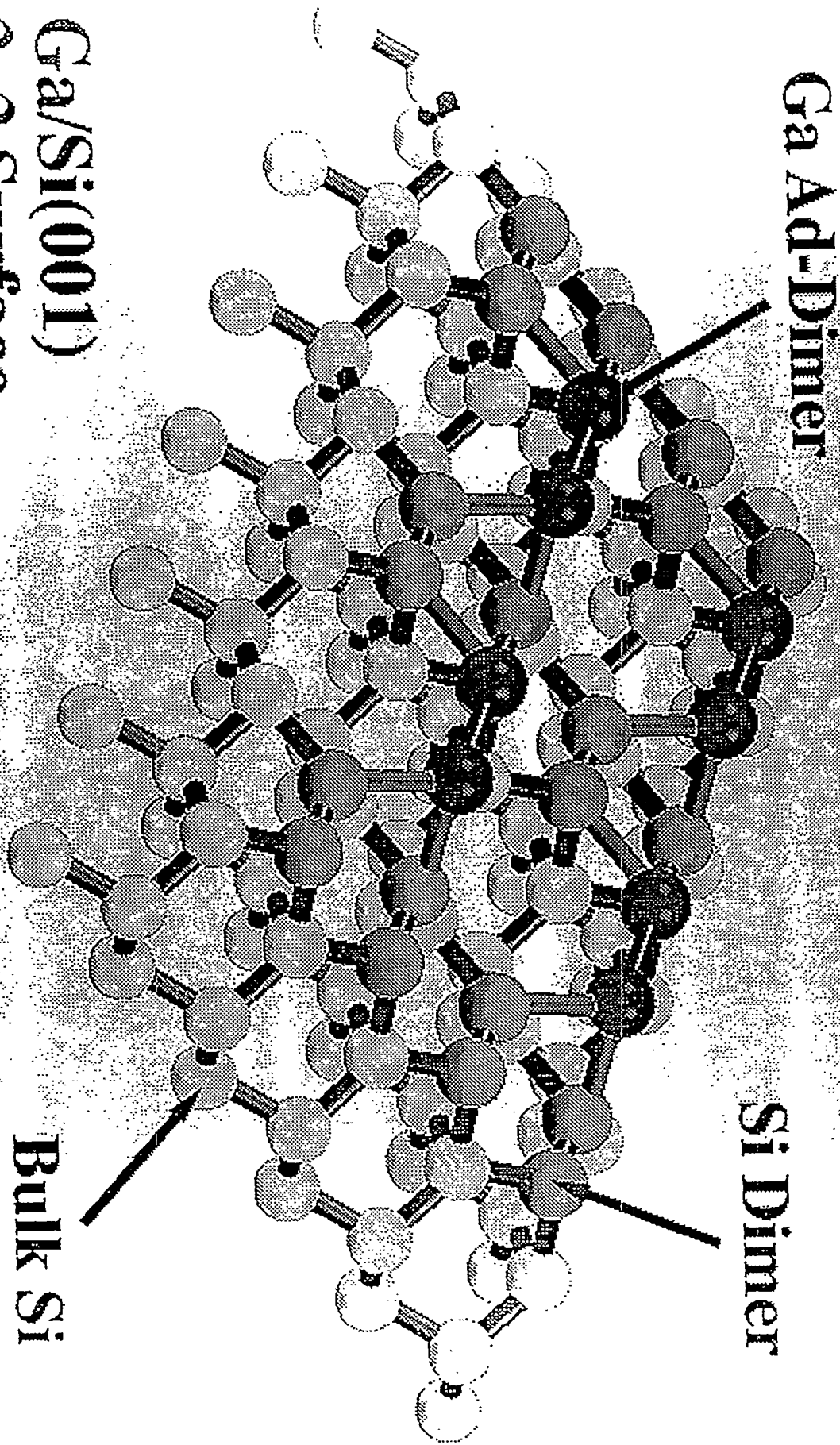
**FIG. 2.** A side view of the Ga/Si(001) surface structure model. The Ga ad-dimer is on top of the underlying Si dimers with its orientation parallel to Si dimers. Long-dash lines are Si(004) lattice planes and short-dash lines are (008) planes.

**FIG. 3.** A schematic drawing of the experimental setup at beamline X15A.

**FIG. 4.** Experimental data (dots) and theoretical curves (solid lines) for the normalized Ga  $K\alpha$  fluorescence yield and Si reflectivity (R) versus Bragg reflection angle  $\theta$  for: (a) the Si(004) reflection and (b) the Si(008) reflection.



Ga/Si(001)  
2x2 Surface



Ga Ad-Dimer

Si Dimer

Bulk Si

Fig. 1

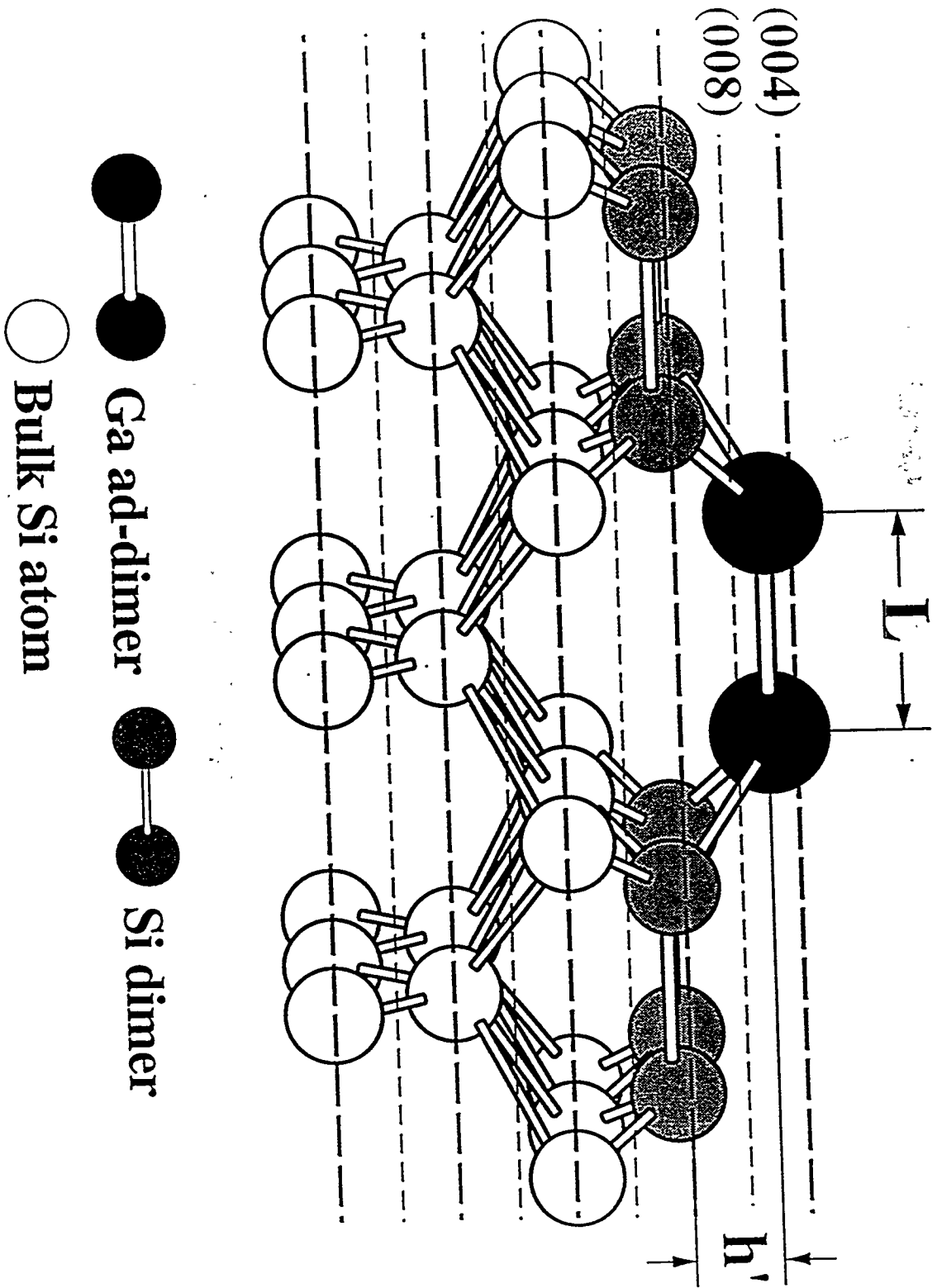


Fig. 2

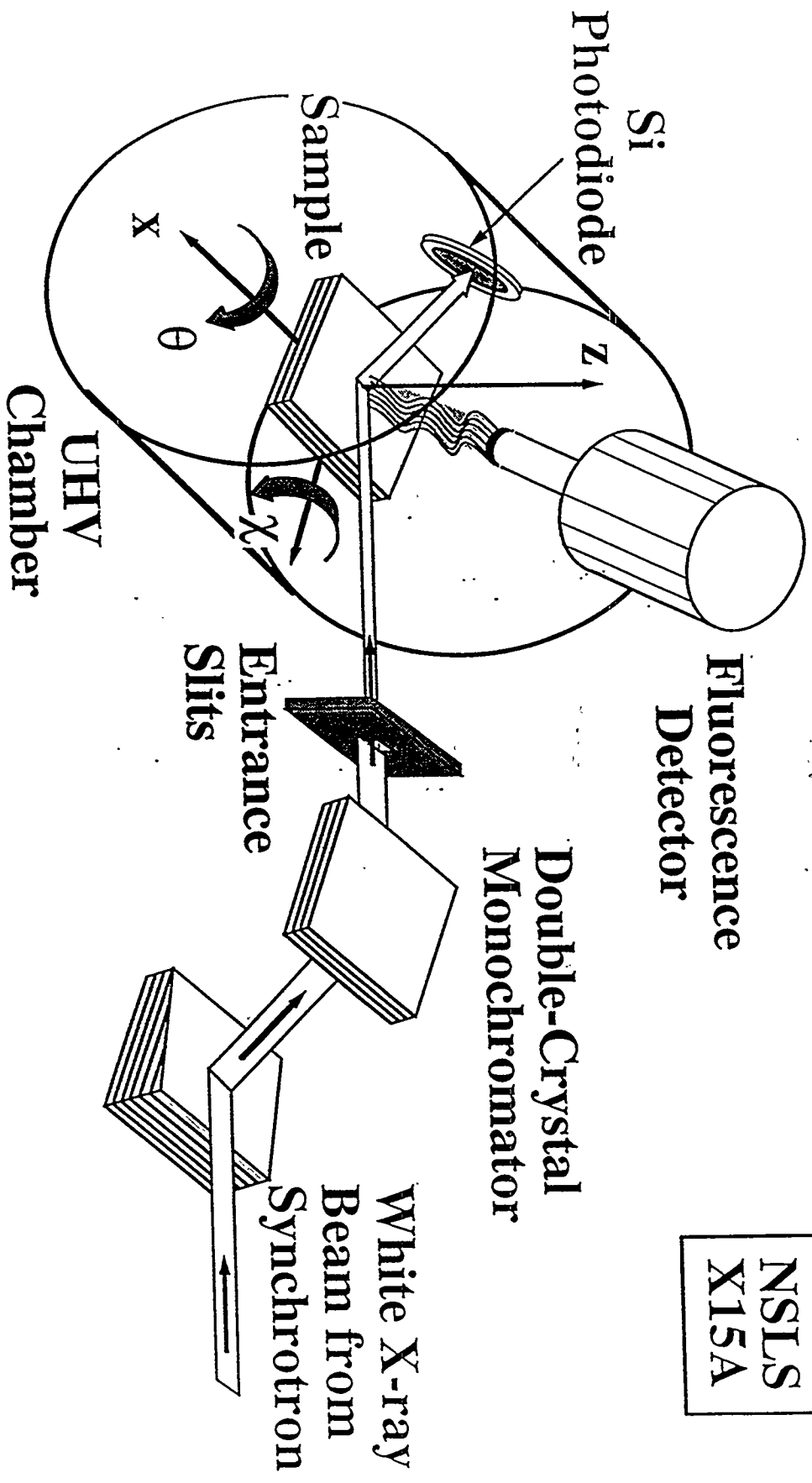


Fig. 3

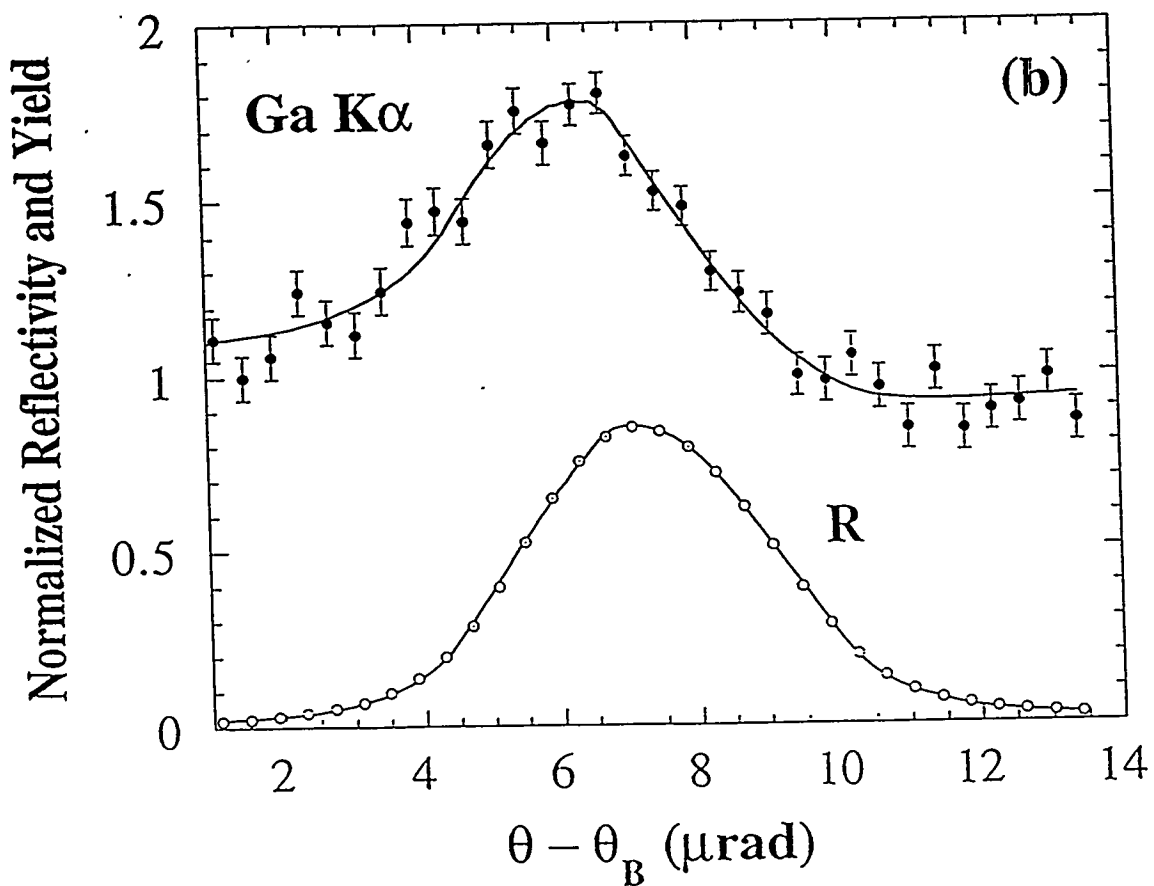
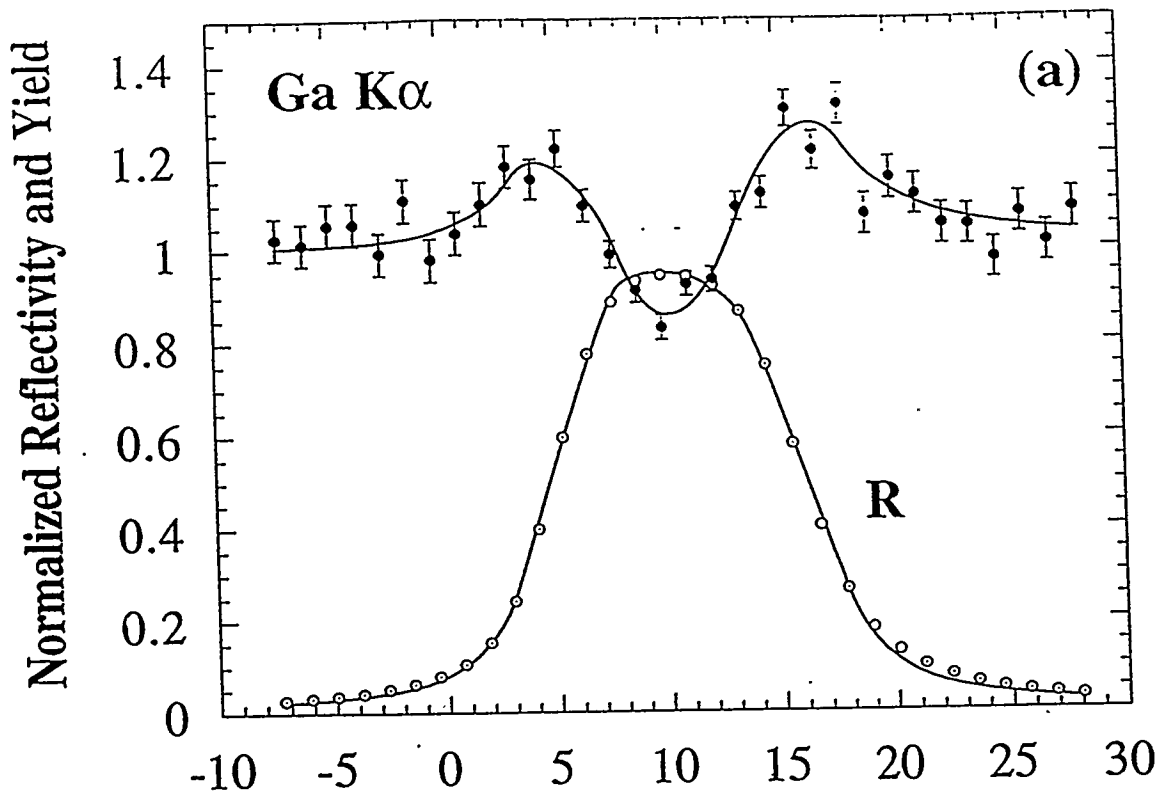


Fig. 4