PHYSICAL REVIEW B **71**, 113314 (2005)

Anisotropy of surface vibration measured by temperature dependence of the spot intensity in reflection high-energy electron diffraction

Mie Hashimoto, Sakura Nishino Takeda, and Hiroshi Daimon
Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama, Ikoma, Nara 630-0192, Japan

(Received 25 October 2004; published 31 March 2005)

A handy method has recently been developed to investigate atomic vibration on a surface using reflection high-energy electron diffraction. We measured the temperature dependence of many spot intensities to obtain the angular dependence of Debye-Waller factors, from which the angular-dependence amplitudes of atomic vibration on surface can be deduced. We applied this method on a Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface. The obtained perpendicular vibrational amplitude of Ga was 0.11 Å, which is in good agreement with those obtained by other works. The lateral vibrational amplitude is 0.07 Å, which was observed directly for the first time.

DOI: 10.1103/PhysRevB.71.113314 PACS number(s): 61.14.−x, 82.45.Jn, 68.47.Fg

Information on the vibration of atoms is important for studying the origin of structural phase transition such as the order-disorder transition or the Peierls transition. For a surface structure, such information has been obtained using surface x-ray diffraction (XRD),[1,2] photoelectron diffraction (PED),[3,4] and low-energy electron diffraction (LEED).[5–8] However, XRD and PED need a Synchrotron Radiation facility and are not convenient for daily use. In these studies the anisotropy of the thermal motion is treated in the multiple scattering formalism. The anisotropy of vibrational amplitude is obtained by fitting the theoretical curve to reproduce the experimental data. So the values are obtained only indirectly. In contrast, as a handy and directly method, we have developed a new method to investigate atomic vibration on a surface using reflection high-energy electron diffraction (RHEED). RHEED is suitable for analyzing the anisotropy of the atom vibration, since its pattern contains many diffraction spots in a much wider (h,k,l) region than XRD or LEED. RHEED is also a very useful tool for the surface structure analysis of several layers below the surface.[9–11] In the present measurement, the one-beam condition,[12] in which the azimuthal angles of the incident beam direction were set at around 7.5° off the $[11\overline{2}]$ direction, was employed in order to avoid the contribution of multiple scattering.

The Si(111) $(\sqrt{3}\times\sqrt{3})$R30°-Ga [from now on denoted as Si(111)$\sqrt{3}\times\sqrt{3}$-Ga] surface is a suitable structure for applying our new technique. The Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface has been investigated extensively[4,13–20] because such a small-unit structure is believed to provide a fundamental understanding of the surface structure formation. At a coverage of 1/3 monolayer (ML) ($1\ \mathrm{ML}=7.83\times10^{14}\ \mathrm{atoms/cm^2}$) gallium atoms are known to occupy the fourfold-coordinated terminal (T_4) site directly above a second-layer Si atom[4,16–20] in a $\sqrt{3}\times\sqrt{3}$ reconstruction on this surface, as shown in Fig. 1. All dangling bonds are saturated in this structure with 1/3 ML coverage.

The structure of this model has been confirmed by previous experimental and theoretical works.[16–20] Vibrational study of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga system has received renewed interest after Martinez *et al.* reported giant adatom vibration at 800 K.[19] The authors measured the vertical positions of Ga atoms relative to the underlying Si layers using the x-ray standing wave (XSW) method, and found that the distribution of Ga heights increased anomalously with temperature. They attributed the anomalous broadening of their data to large vibrational amplitudes of the adatoms, and predicted a pronounced decrease of the corresponding vibrational frequency with increasing temperature. The root-mean-square projection of displacements (RMSPRD's) of Ga adatom at room temperature has been measured experimentally to be about >0.1 Å. This value can be compared with 0.14 Å measured by the kinetic-energy dependence of the PED,[4] and 0.11 Å obtained by high-resolution electron-energy-loss spectroscopy (HREELS).[20] Note that these values are vertical (XSW) or directionally averaged (PED and HREELS) amplitudes, and anisotropy at around room temperature has not yet been measured.

In the present paper, we studied the anisotropy of atomic vibrational amplitude on the surface using RHEED. We developed a method to measure the temperature dependence of many spot intensities to obtain the angular dependence of the Debye-Waller factor, from which the angular-dependent amplitudes of atomic vibration on surfaces can be deduced. We applied this method to the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface.

The reflected RHEED spot intensity $\langle I\rangle_T$ at the scattering

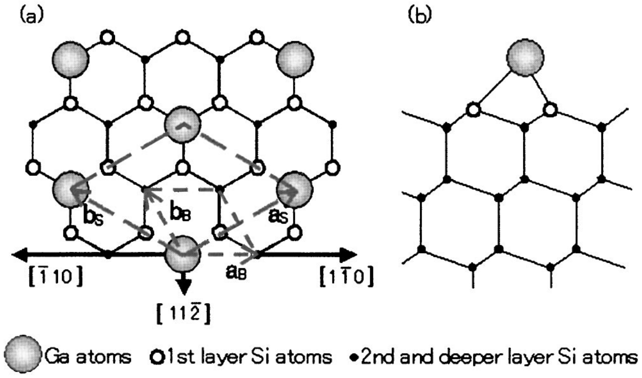

FIG. 1. (a) Top view and (b) side view of the T_4 model for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface. 1×1 and $\sqrt{3}\times\sqrt{3}$ unit meshes are shown by short and long dashed lines, respectively. $\mathbf{a}_B$ and $\mathbf{b}_B$ are unit vectors for the 1×1 structure and $\mathbf{a}_S$ and $\mathbf{b}_S$ are for the $\sqrt{3}\times\sqrt{3}$ structure.

1098-0121/2005/71(11)/113314(4)/$23.00

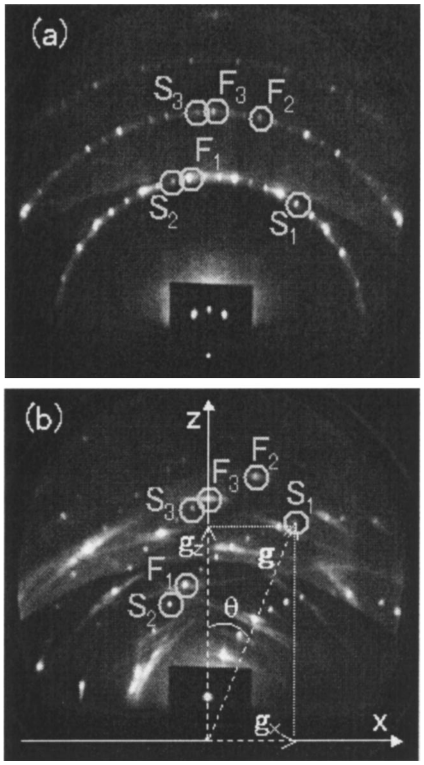

FIG. 2. (a) RHEED pattern of $[11\bar{2}]$ incidence and (b) of one-beam condition. F_1, F_2, and F_3 indicate fundamental spots and S_1, S_2, and S_3 indicate $\sqrt{3}\times\sqrt{3}$ superstructure spots.

vector (the vector difference of the wave vector of the reflected wave and the incident wave) **g** is derived from the kinematic formula as[21]

$$\langle I\rangle_T \propto |t(\mathbf{g})|^2 \exp(-2M), \tag{1}$$

where $t(\mathbf{g})$ is a scattering factor and $\exp(-2M)$ is the Debye-Waller factor. M is expressed by the formula[21]

$$M = \frac{1}{2}\frac{3\hbar^2|\mathbf{g}|^2}{2mk_B\Theta^2}T, \tag{2}$$

where m is the mass of the atom, k_B is Boltzmann's constant, T is the temperature in K, and Θ is the Debye temperature.

Consider a spot at a particular **g** in a direction θ from surface normal, as shown in Fig. 2. Because g_y is small in comparison with g_x or g_z in this case, we neglect g_y in this paper for simplicity,

$$\mathbf{g} = (g_x, g_y, g_z) \cong (g_x, 0, g_z) = |\mathbf{g}|(\sin\theta, 0, \cos\theta). \tag{3}$$

M is proportional to T, and the spot intensity decreases exponentially with increasing T. When we plot the temperature dependence of the intensity of the spot in a legalistic scale, it becomes a linear line. The slope of the line $M^\circ(g,\theta)$ is expressed using Eqs. (1) and (2) as

$$M^\circ(g,\theta) = \frac{3\hbar^2|\mathbf{g}|^2}{2mk_B\Theta^2} = \frac{2M}{T}. \tag{4}$$

The M is expressed in another form using the displacement of atoms **u** around their mean position as[21]

$$M = \frac{1}{2}\langle[\mathbf{g}\cdot\mathbf{u}]^2\rangle_T. \tag{5}$$

Here, $\langle[\mathbf{g}\cdot\mathbf{u}]^2\rangle_T$ means the average over time at a temperature T. We define

$$\mathbf{u} = (u_x, u_y, u_z)\cos(\omega t). \tag{6}$$

Here atomic motion is simplified as a harmonic oscillator with an amplitude vector **u** and frequency ω. Then from Eqs. (3) and (6)

$$\begin{aligned}\langle[\mathbf{g}\cdot\mathbf{u}]^2\rangle_T &= \langle|\mathbf{g}|^2(u_x\sin\theta + u_z\cos\theta)^2\cos^2(\omega t)\rangle_T \\ &= \frac{1}{2}|\mathbf{g}|^2(u_x\sin\theta + u_z\cos\theta)^2. \end{aligned}\tag{7}$$

Here we define the "angular-dependent amplitude factor" $u(\theta)$ as

$$u(\theta) \equiv u_x\sin\theta + u_z\cos\theta. \tag{8}$$

By using Eqs. (4), (5), (7), and (8), we obtain

$$u(\theta) = \frac{\sqrt{2M^\circ T}}{|\mathbf{g}|}. \tag{9}$$

The procedure for obtaining the components of vibrational amplitudes, u_x and u_z, is the following.

(1) From the temperature dependence of intensity of the spot at (g,θ) we obtain the slope $M^\circ(g,\theta)$.

(2) $u(\theta)$ for many spots are plotted against θ using Eq. (9).

(3) By fitting the $u(\theta)$ data by a curve $u_x\sin\theta + u_z\cos\theta$ we can obtain the horizontal and vertical components u_x and u_z of atomic vibration.

The specimen used was a mirror-polished, 1.5–3.0 Ω cm, n-type Si(111) wafer. The surface of the specimen was cleaned by heating at 1250 °C in 8×10^{-11} Torr. Gallium (Ga) atoms were evaporated from a crucible. The $\sqrt{3}\times\sqrt{3}$ structure was prepared by the deposition of Ga at the rate of about 1/6 ML/min onto the 7×7 clean surface held at 550 °C. The coverage of the Ga atoms was monitored by RHEED. The intensities of the 7×7 superstructure spots were observed as a function of Ga deposition time. Some superstructure spots temporarily increased their intensities during Ga deposition and then decreased. Other spots monotonically faded out. When all 7×7 spots faded out and the $\sqrt{3}\times\sqrt{3}$ spots intensity showed its maximum, we regarded the Ga coverage as 1/3 ML. The kinetic energy of the incident beam was set at 15 keV. The glancing angle of the incident beam was set at 0.9°. We measured the temperature dependence of the intensity of RHEED spots from room temperature to 100 K.

RHEED patterns from Si(111)$\sqrt{3}\times\sqrt{3}$-Ga are shown in Fig. 2. Azimuthal angles are along $[11\bar{2}]$ for (a) and 7.5° off from $[11\bar{2}]$ for (b), which is called the one-beam condition.[12] We have chosen the one-beam condition so that multiple scattering minimizes and the kinematic theory holds. The temperature of the sample for these RHEED patterns was 100 K. The circles show some of the spots used for the present analysis. Fundamental spots corresponding to Si(111)

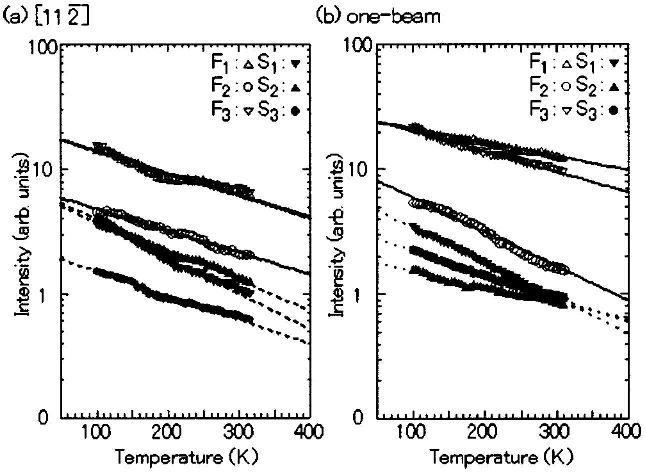

FIG. 3. (a) Temperature dependence of spot intensities in $[11\bar{2}]$ incidence and (b) in one-beam condition. Lines are obtained by fittings using Eq. (1).

1×1 periodicity are indicated by F_1, F_2, and F_3 in the figure. Because the intensity of the spots at Laue zones higher than second decreases rapidly with increasing sample temperature, and because they are weak at room temperature, we avoided using those spots for the analysis. We took many RHEED patterns, changing the sample temperature, and investigated the temperature dependence of each spot intensity.

Figure 3 shows some of such temperature dependences of spot intensities from the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface. Intensities are obtained by integration over a certain area which covers each spot followed by subtraction of the background intensity. Background intensities are calculated from the intensity in a region which surrounds the area used for corresponding spot intensity calculation. Reduction of atomic vibration at lower temperature increases spot intensity according to Eq. (1). Although all spot intensities increase with decreasing temperature, the slope is larger for spots with larger $|\mathbf{g}|$. The slopes M° for each spot were obtained by linear fitting in the log scale graph. From these values, two orthogonal components (u_x, u_z) of atomic vibration are obtained following the procedure explained previously. Angular dependent amplitude factor $u(\theta)=\sqrt{2M^\circ T/|\mathbf{g}|}$ at $T=300$ K is shown in Fig. 4. The $u(\theta)$ for $[11\bar{2}]$ direction and one-beam condition are shown by triangles and circles, respectively. Within each condition, open and filled marks are for the fundamental spots and superstructure spots, respectively.

Solid curves in the figure are obtained by fitting to the data of the one-beam condition with Eq. (8). Dashed-dotted lines show the components $u_z\cos\theta$ and $u_x\sin\theta$. The crossing points at $\theta=0°$ and 90° give the two vibrational amplitude components u_z and u_x, respectively. Thus the perpendicular vibrational amplitude u_z of the Ga atoms is obtained as 0.14 Å at 300 K, and the lateral vibrational amplitude u_x was obtained as 0.07 Å, as shown in Table I. This value is in good agreement with $u_z>0.1$ Å by XSW.[19] The lateral vibrational amplitude at room temperature was obtained directly for the first time. The average isotropic vibrational amplitude was estimated by $\sqrt{(u_z^2+2u_x^2)/3}$ as 0.10 Å. This value is in good agreement with 0.14 Å by PED[4] and 0.11 Å by HREELS.[20]

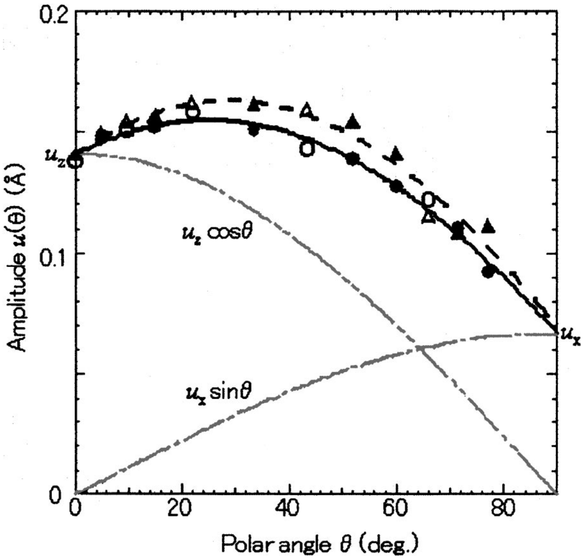

FIG. 4. Angular dependent amplitudes factor obtained from $[11\bar{2}]$ direction (triangles) and one-beam condition (circles). Filled and open symbols are for fundamental and superstructure spots, respectively. The solid line and dashed line are obtained by fitting using Eq. (8). The gray lines are components $u_z\cos\theta$ and $u_x\sin\theta$.

The dashed line is the fitting result in the $[11\bar{2}]$ direction. There is only a little difference in u_z and u_x values between those obtained from the $[11\bar{2}]$ direction and the one-beam condition, although more multiple scattering effect is expected in the $[11\bar{2}]$ direction than the one-beam condition because of the symmetric character. This small difference indicates that multiple scattering (or dynamical) effect is small and the kinematical theory holds in these conditions. This is probably because we choose a glancing angle where no surface wave resonance occurs.

The small incidence angle of 0.9° and the heavy mass of Ga atom could reduce bulk contribution in this work. The bulk (Si) contribution was estimated to be about 30% assuming the mean free path of 50 Å, the incidence angle of 0.9°, the diffracted angle 7°, and the inner potential of 12 eV.[14] Because superstructure spots are produced only from the surface $\sqrt{3}\times\sqrt{3}$ structure while fundamental spots contain information on both the $\sqrt{3}\times\sqrt{3}$ and the underlying bulk 1×1-Si structures, they could give a different vibrational amplitude. But as shown in Fig. 4, fundamental spots and superstructure spots gave the same result. This means that bulk (Si) contribution is smaller than expected. Hence the obtained u_z and u_x can be considered to be mainly the vibrational amplitude of Ga atoms.

TABLE I. Vibrational amplitude of Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface at room temperature obtained by various experimental methods.

	RHEED (This work)	XSW (Ref. 19)	PED (Ref. 4)	HREELS (Ref. 20)
u_z	0.14 Å	>0.1 Å		
u_x	0.07 Å			
u_{average}	0.10 Å		0.14 Å	0.11 Å

A method of measuring the anisotropy of surface vibrational amplitude was developed using temperature dependence of RHEED spot intensity. The amplitudes of Ga atomic vibration in Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface was obtained as 0.14 Å for the perpendicular direction and 0.07 Å for the horizontal direction. The value for the perpendicular direction was in good agreement with other works. Anisotropy on surface vibration was observed.

---

[1] T. Takahashi, H. Tajiri, K. Sumitani, K. Akimoto, H. Sugiyama, X. Zhang, and H. Kawata, Surf. Rev. Lett. **10**, 519 (2003).

[2] H. Tajiri, K. Sumitani, S. Nakatani, A. Nojima, T. Yakahashi, K. Akimoto, H. Sugiyama, X. Zhang, and H. Kawata, Phys. Rev. B **68**, 035330 (2003).

[3] V. Fritzsche, K.-M. Schindler, P. Gardner, A. M. Bradshaw, M. C. Asensio, and D. P. Woodruff, Surf. Sci. **269/270**, 35 (1992).

[4] T. Hanada, H. Daimon, S. Nagano, and S. Ino, S. Suga, and Y. Murata, Phys. Rev. B **55**, 16 420 (1997).

[5] H. Over, W. Moritz, and G. Ertl, Phys. Rev. Lett. **70**, 315 (1993).

[6] U. Löffler, U. Muschiol, P. Bayer, K. Heinz, V. Fritzsche, and J. B. Pendry, Surf. Sci. **331**, 1435 (1995).

[7] J. Landskron, W. Moritz, B. Narloch, G. Held, and D. Menzel, Surf. Sci. **441**, 91 (1999).

[8] W. Moritz and J. Landskron, in *Solid-State Photoemission and Related Methods*, edited by W. Schattke and M. A. Van Hove (Wiley-VCH, New York, 2003), Chap. 16, pp. 433–459.

[9] A. Ichimiya, S. Kohmoto, T. Fujii, and Y. Horio, Appl. Surf. Sci. **41/42**, 82 (1989).

[10] T. Hanada, S. Ino, and H. Daimon, Surf. Sci. **313**, 143 (1994).

[11] Y. Fukaya and Y. Shigeta, Phys. Rev. B **65**, 195415 (2002).

[12] A. Ichimiya, Surf. Sci. **192**, L893 (1987).

[13] K. Higashiyama, S. Kono, and T. Sagawa, Surf. Sci. **175**, L794 (1986).

[14] T. Hanada, H. Daimon, and S. Ino, Phys. Rev. B **51**, 13 320 (1995).

[15] J. M. Nicholls, B. Reihl, and J. E. Northrup, Phys. Rev. B **35**, 4137 (1987).

[16] J. Nogami, S. Park, and C. F. Quate, Surf. Sci. **203**, L631 (1988).

[17] J. Zegenhagen, J. R. Patel, P. Freeland, D. M. Chen, J. A. Golovchenko, P. Bedrossian, and J. E. Northrup, Phys. Rev. B **39**, 1298 (1989).

[18] A. Kawazu and H. Sakama, Phys. Rev. B **37**, 2704 (1988).

[19] R. E. Martinez, E. Fontes, J. A. Golovchenko, and J. R. Patel, Phys. Rev. Lett. **69**, 1061 (1992).

[20] J. Schmidt, H. Ibach, and J. E. Muller, Phys. Rev. B **51**, 5233 (1995).

[21] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974).