RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 5 15 AUGUST 1989-I

Surface roughness and correlation length determined from x-ray-diffraction line-shape analysis on germanium (111)

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(Received 11 April 1989)

An x-ray-diffraction experiment performed on a germanium (111) crystal shows both rodlike and diffuselike scattering from the surface on a nonspecular crystal truncation rod. These scattering contributions are explained using existing theory on surface roughness. Two treatments to the Ge(111) surface have been used to provide examples with different roughness characteristics for this study. The magnitude of the roughness and the lateral scale of surface flat regions are obtained for both cases.

It has been known that roughness on crystal surfaces can be studied by x-ray-diffraction technique with monolayer sensitivity, from measurements on the so-called crystal truncation rods (CTR).[1,2] The intensity in these rods arises from the abrupt termination of bulk materials at the surface. For a perfectly truncated flat crystal surface, the truncation rod is an exact two-dimensional δ function (rodlike) with a structure factor $F_{\mathrm{CTR}}=1/\sin(Q_z c)$, where Q_z is the perpendicular momentum transfer and c is the lattice constant normal to the surface.[2] As pointed out by several authors,[1,3,4] when the surface is rough, the diffracted intensity consists of two parts:

$$I(\mathbf{q})=|F_c F_{\mathrm{CTR}}|^2\{g(q_z)\delta(\mathbf{q}_r)+h(\mathbf{q}_r,q_z)[1-g(q_z)]\}\,. \tag{1}$$

[$h(\mathbf{q}_r,q_z)$ is peaked at $\mathbf{q}_r=0$ and $\int h(\mathbf{q}_r,q_z)d\mathbf{q}_r=1$, where $\mathbf{q}_r$ and q_z are the momentum transfers parallel and normal to the surface, respectively, measured from the nearest bulk Bragg point; F_c is the unit-cell structure factor.] The true truncation rod intensity, namely the δ-function term, is multiplied by a Debye-Waller-like factor $g(q_z)$, which is the Fourier transform of the surface height probability distribution function $P(z)$; this causes the intensity to decay faster with increasing q_z than for a perfectly sharp interface. In addition, because of the decrease in long-range order brought about by random surface steps, there is a broad diffuse scattering peak around the truncation rod, represented by $h(\mathbf{q}_r,q_z)$, which is basically the Fourier transform of the surface height-height correlation function $C(\mathbf{r})\equiv\langle z(\mathbf{r})z(\mathbf{0})\rangle$, when the rms roughness is small compared to $1/q_z$. Alternatively, the diffuse scattering can be viewed to be produced by surface gratings and its intensity is proportional to the so-called power spectrum density which is related to the correlation function $C(\mathbf{r})$ by a Fourier transform.[5-7]

For the specular rod near the origin (Fresnel reflectivity region), extensive studies on both the rod and the diffuse scattering on x-ray mirrors and liquid-crystal surfaces can be found in the literature.[4-9] For nonspecular truncation rods, however, very few experimental results on the diffuse scattering part have been reported.[10] In this paper, we present an x-ray-diffraction experiment on a Ge(111) single crystal, in which we have observed both the rod and the diffuse contributions to the scattered intensity near a nonspecular crystal truncation rod. We will demonstrate the importance of the diffuse scattering and show how it helps to determine the surface roughness in both the normal and lateral directions.

The experiment was performed at the C2 Station of the Cornell High Energy Synchrotron Source. A flat and a saggital focusing Si(111) crystal were used to provide monochromatic radiation of wavelength 1.459 Å, with higher-order harmonics eliminated by a flat quartz mirror. The incident beam was reduced to 2 mm horizontally by 0.7 mm vertically by slits and monitored with an ionization chamber. The diffracted beam was measured by a NaI detector, with its in-plane resolution $\Delta q_{2\theta}=0.022$ Å^{-1} for the full width at half maximum (FWHM), as determined by a 5-mrad Soller slit. The resolution perpendicular to the vertical diffraction plane was 0.15 Å^{-1} (FWHM), due to the horizontal divergence of the incident beam and a 1.2-cm horizontal detector slit. The transverse resolution of $\Delta q_\theta=0.00025$ Å^{-1} was dominated by the vertical divergence of the incident beam, which was measured by a θ scan on the weak Ge(222) forbidden bulk reflection and found to be 15 arc-sec (FWHM). It was this high resolution that allowed our line-shape analysis, while the relatively low resolutions in the other two directions actually helped the observation of the diffuselike scattering since the arrangement effectively integrated the diffuse peak perpendicular to the rocking scan direction.

The Ge(111) sample with a surface area of 2.0×1.4 cm^2 was mounted at the center of a standard four-circle diffractometer, operated in its symmetric mode ($\omega=0$). The sample was cut with its surface parallel ($<0.1°$) to the (111) atomic planes and was aligned in such a way that the (111) reciprocal vector coincides with the ϕ axis of the diffractometer. The sample had been pretreated by Syton polishing, sputtering and annealing under ultrahigh vacuum conditions, and then exposed to air for about two months. Two sets of data were obtained on the same sample: one with the sample as described (case A), and the other after the sample was treated by a hydrofluoric-acid etch, followed by an iodine-methanol nonabrasive pad polishing procedure,[11] and then put into a helium gas envi-

ronment (case B). The wet chemistry treatment causes the Ge surface to be passivated by iodine.

A convenient hexagonal reciprocal unit cell is adopted, with $(300)_h=(22\bar{4})_c$, $(030)_h=(\bar{2}4\bar{2})_c$, $(003)_h=(111)_c$, so that a perpendicular momentum transfer is represented by a single Miller index l. The measurements were done mainly on the $(10)_h$ truncation rod, the one connecting the $(11\bar{1})_c$ and $(220)_c$ bulk reflections. At each l along the rod, a transverse rocking curve was measured with a fixed 2θ detector position. A typical counting time at each θ step was 2 sec, with an incident flux of 4×10^9 photons per second.

A series of typical rocking-curve scans are shown in Fig. 1, for both cases A and B. After subtracting a constant background, which is mainly due to thermal diffuse scattering, we found that the line shape of each rocking curve could be described by a sum of two Lorentzians, one sharp and the other broad. The sharp Lorentzian is from the true rodlike scattering, whose finite width is due to the combined effects of instrumental resolution, surface domain size, and domain misorientation. The averaged values of the χ^2 fitted FWHM's are 0.028° for case A and 0.070° for case B, which yield minimum surface domain sizes of ~1100 and ~450 Å, respectively. In both cases, the instrumental resolution is sufficiently good (~0.004°) and can be neglected. We believe that the smaller domain size or the greater misorientation in case B is due to the fact that the sample was not annealed after the wet chemistry treatment.

The broad Lorentzian is due to the diffuselike scattering represented by $h(\mathbf{q}_r,q_z)$ in Eq. (1). It can be shown that an isotropic exponential correlation function $C(\mathbf{r})=\exp(-r/L)$ has a Fourier transform which is a Lorentzian in reciprocal space, with a FWHM of $\Delta q_x=2/L$, if one integrates over the q_y direction, i.e.,

$$h(\mathbf{q}_r,q_z)=\int dq_y\int \exp\left[-\frac{r}{L}+i\mathbf{q}_r\cdot\mathbf{r}\right]d\mathbf{r}=\frac{4\pi/L}{q_x^2+1/L^2}\,. \tag{2}$$

The integration over q_y is effectively done in the experiment because of the broad resolution function perpendicular to the q_x (θ scan) direction. We found that this simple function can fit the data in case B very well, with a surface height-height correlation length $L=100$ Å. In case A, however, the rocking curve data show that Δq_x is not a constant along the rod and in fact is approximately proportional to q_z, so that it diverges when moving away from a Bragg point. This behavior is qualitatively in agreement with two separate surface statistical models proposed by Andrews and Cowley,[1] and by Sinha *et al.*,[4] but no quantitative analysis was attempted. If we nevertheless use the same fitting procedure as for case B, we obtain a rough estimate of the height-height correlation length $L\sim200$ Å from the half width at half maximum equal to 0.15° of the broad Lorentzian at $l=0.5$.

Equations similar to Eq. (1) have also been used to interpret experimental results in low-energy electron diffractions from rough crystal surfaces.[12,13] According to this theory, the diffuse scattering arises from surface terraces with a variety of lengths, characterized by a terrace length distribution with an average length $\langle L\rangle$. In fact, the simple exponential correlation function $C(r)=\exp(-r/L)$ is directly related to the so-called two-level geometric distribution of terrace lengths with $\langle L\rangle=2L$.[12] Therefore, twice the correlation length $2L$ gives a direct measure of the average flat region size on the surface, and the value for case A is $2L\sim400$ Å and for case B is $2L\sim200$ Å.

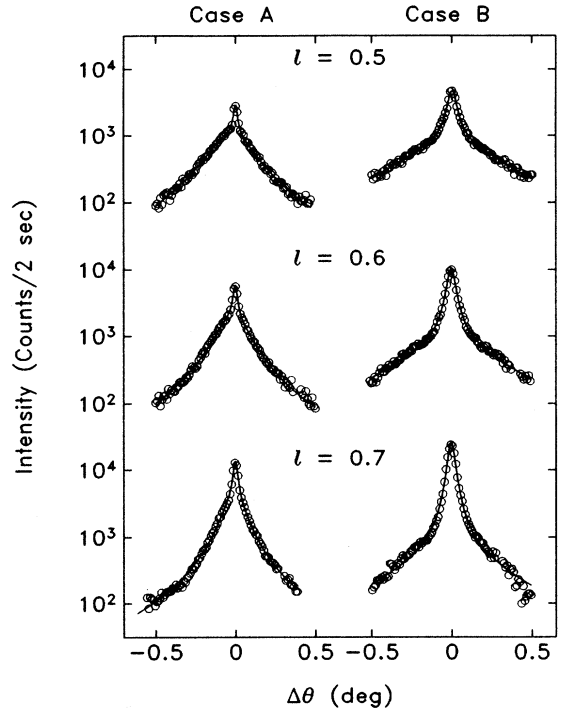

FIG. 1. Rocking scans transverse to the crystal truncation rod $(10l)_h$, for cases A and B, at $l=0.5$, 0.6, and 0.7. The open circles are experimental data points and the solid lines are the χ^2 fits using two Lorentzians. The thermal diffuse scattering background has been subtracted out on each plot.

From Eq. (1) it may be noticed that the normalized diffuselike intensity, $\beta(q_z)$, defined as the ratio of the integrated intensity of the diffuselike scattering to that of the rodlike scattering, is related only to the surface height Fourier transform $g(q_z)$,

$$\beta(q_z)\equiv\frac{I_{\rm diff}}{I_{\rm rod}}=\frac{1}{g(q_z)}-1\,, \tag{3}$$

which is independent of the structure factors $F_cF_{\rm CTR}$ and the lateral correlation function that is involved in $h(\mathbf{q}_r,q_z)$.[14] Therefore, by analyzing β as a function of q_z, the functional form of $g(q_z)$ and a parameter related to the mean-square surface roughness can be deduced. Such a plot around the $(101)_h$ point is shown in Fig. 2 for both cases A and B. We found that either $g(q_z)=\exp(-\sigma^2q_z^2)$, which is the Fourier transform of a Gaussian distribution $P(z)=\exp(-z^2/\sigma^2)$, or $g(q_z)=(1+\zeta^2q_z^2)^{-2}$, which is the transform of a simple exponential $P(z)=\exp(-|z|/\zeta)$, can fit the data fairly well, the fit with simple exponential being slightly better.

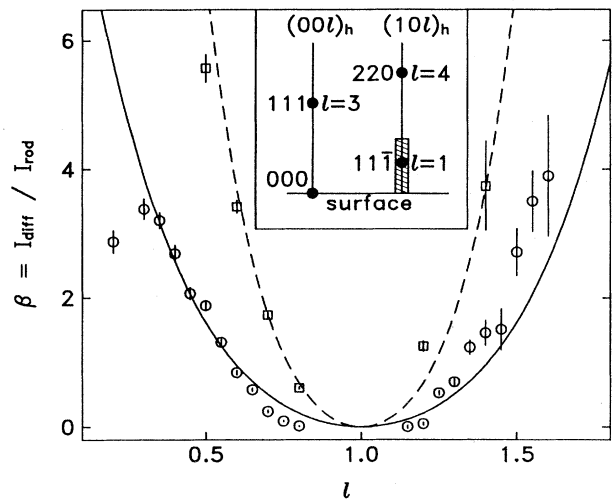

FIG. 2. Intensity ratio $\beta = I_{\rm diff}/I_{\rm rod}$ as a function of perpendicular momentum transfer q_z on the nonspecular rod $(10l)_h$. The experimental data are plotted as open circles for case B and squares for case A. The curves are the calculations using $\beta(q_z) = (1+\zeta^2 q_z^2)^2 - 1$, with $\zeta = 4.3$ Å (dashed line) for case A and $\zeta = 2.5$ Å (solid line) for case B. Note that no corrections for surface area and other scattering geometry related factors are necessary because of the normalized ratio β. The shaded region in the inset shows the locations of the experimental points in reciprocal space.

The two curves in Fig. 2 are the best fits to the data using $g(q_z) = (1+\zeta^2 q_z^2)^{-2}$, with $\zeta = 4.3 \pm 0.5$ Å for case A (dashed line) and $\zeta = 2.5 \pm 0.3$ Å for case B (solid line). Clearly, the wet chemistry treatment to the sample has yielded a much flatter crystal surface. This type of atomic-scale flatness on semiconductor surfaces after this treatment has been previously inferred from spectroscopic ellipsometry observations.[11] It should be noted that because the measurements involve large momentum transfers on a nonspecular rod, the surface that the x rays are probing is actually the interface between the amorphous oxide layer and the crystal structure underneath.

Surface roughness could also be modeled from the total integrated intensity

$$I_{\rm tot}(q_z) = I_{\rm rod} + I_{\rm diff} = |F_c F_{\rm CTR}|^2$$

by inclusion of incomplete layers in $F_{\rm CTR}$. However, in this description one loses the information on the lateral scale of the roughness. In our analysis the magnitude of surface roughness and the lateral scale of flat regions are treated as two independent aspects of surface morphology. The surface in case A has a larger roughness magnitude ζ than in case B, but it is actually "smoother" in the lateral scale because of its greater correlation length L. This kind of distinction may be important in applying measurements of the type reported here to the study of thermal roughening transitions on crystal surfaces.[10,15]

In summary, we have demonstrated that measurements of the diffuselike x-ray scattering in rocking scans transverse to a nonspecular crystal truncation rod allow a determination of the scale of the surface or interface roughness in lateral directions. The intensity ratio of the diffuselike to the rodlike scattering has been used to extract the magnitude of the roughness perpendicular to the surface. A Ge(111) surface, treated in two different ways, has been used as examples for the study. For the Ge crystal covered with a naturally grown oxide layer, the surface roughness was found to be 4.3 ± 0.5 Å on a lateral scale of about 400 Å, and for the clean Ge crystal surface passivated with iodine, the roughness was 2.5 ± 0.3 Å on a lateral scale of 200 Å. We have also shown that the lateral scale of the roughness can be related to the average terrace length on the rough crystal surface. Complementary studies with the scanning tunneling microscope, for example, to verify the microscopic interpretation of these statistical roughness parameters would be very interesting.

We are grateful to the technical staff at the Cornell High Energy Synchrotron Source for assistance during our experiment. This work is supported by the National Science Foundation through the Materials Science Center at Cornell University and the Cornell High Energy Synchrotron Source, via Grants No. DMR85-16616 and No. DMR87-19764. Support from the Semiconductor Research Corporation is also acknowledged.

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