Acta Cryst. (1990). A**46**, 83-86

Surface Structure Analysis by Transmission Electron Diffraction: Effects of the Phases of Structure Factors

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(*Received* 15 *March* 1989; *accepted* 21 *July* 1989)

Abstract

To solve the problems related to the phases of the structure factors in surface structure analysis by transmission electron diffraction, the dynamical diffraction in the bulk crystal underneath the surface layer is considered by the many-beam theory. In the case of normal beam incidence, the intensities of superlattice reflections from surfaces and/or adsorbed layers are used to discriminate whether the surface structure is substitutional or displacive in type. In the case where only two beams are strongly excited in the bulk crystal, the phases of the structure factors of the surface layer are determined by the rocking curve of the superlattice reflections.

1. Introduction

In previous papers transmission electron diffraction (TED) was used to determine the dimer adatom stacking-fault (DAS) model for the 7×7 reconstructed structure of the Si(111) surface (Takayanagi, Tanishiro, M. Takahashi & S. Takahashi, 1985; Takayanagi, Tanishiro, S. Takahashi & M. Takahashi, 1985). The intensities of the superlattice spots were analyzed by kinematical theory, where the incident-beam direction was chosen so that no Bragg reflections were excited strongly in the bulk crystal. To obtain the kinematical intensities, however, we averaged the intensities of the reflections which are related to each other with the C_{6v} symmetry of the reconstructed structure. These reflections had different intensities because of dynamical diffraction in the bulk crystal underneath the reconstructed surface, as also shown theoretically (Tanishiro & Takayanagi, 1989) by performing the multislice calculation (dynamical calculation) (Cowley, 1975).

In an early work by Kambe (1957) it is shown that the intensities of transmitted and diffracted waves depend on the relative phase difference $\varphi_{\mathbf{g}}-\varphi_{\mathbf{g}'}+\varphi_{\mathbf{g}-\mathbf{g}'}$ of the structure factors for the three reflections $\mathbf{g}$, $\mathbf{g}'$ and $\mathbf{g}-\mathbf{g}'$ excited simultaneously in the bulk crystal. His theory indicates that the phases of superlattice reflections from the surface layer may be determined by using the dynamical diffraction effect in the bulk crystal underneath the surface layer. With the information of phases of some of the superlattice reflections, we can determine the surface structure with certainty.

In this paper, we derive analytical expressions of the intensity of the superlattice reflections of reconstructed and/or adsorbed layers by the many-beam dynamical theory in the case of normal beam incidence and the two-beam case. Methods to determine the phase relations between the structure factors by utilizing the dynamical diffraction effect are proposed. Also a method to discriminate between structures of substitutional and displacive types is proposed.

2. General formulation

We consider the case where the surface layer is on the bottom side of the crystal of thickness z, and the top surface is chosen to be the plane $z=0$ (see Fig. 1). Provided that the plane wave with unit amplitude, $\Psi(\mathbf{K}_0)=\exp\{i\mathbf{K}_0\cdot\mathbf{z}\}$ is incident on the top surface, the wave function at the bottom surface of the bulk is given according to the many-beam dynamical theory (Howie, 1970) by

$$\psi(\mathbf{k}_0)=\sum_{\mathbf{g}} u_{\mathbf{g}}(\mathbf{k}_0)\exp[i(\mathbf{k}_0+\mathbf{g})\cdot\mathbf{r}]. \qquad (1)$$

The amplitude of the diffracted wave with reflection vector $\mathbf{g}$ is then given by

$$u_{\mathbf{g}}=\sum_{j} C_0^{(j)*}\exp[ik_z^{(j)}z]C_{\mathbf{g}}^{(j)}, \qquad (2)$$

where $k_z^{(j)}$ and $C_{\mathbf{g}}^{(j)}$ $(j=1,2,\ldots,N)$ are the eigenvalue and eigenvector of the jth branch for the secular

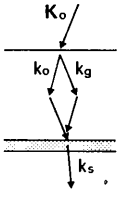

Fig. 1. The case that the reconstructed surface layer is at the lower side of the crystal. The transmitted and Bragg-reflected waves are diffracted kinematically in the surface layer.

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equation

$$[-k_z^{(j)}+s_g]C_g^{(j)}+\sum_h U_{g-h}C_h^{(j)}=0. \quad (3)$$

In (3), U_g [$U_g=V_g/2k_{z0}$ ($2m/\hbar^2=1$)] is the Fourier coefficient of the scattering potential and s_g is the excitation error defined by

$$s_g=(\mathbf{T}\cdot\mathbf{g}-g^2/2)/k_{z0},$$

where $\mathbf{k}_{z0}$ and $-\mathbf{T}$ are the normal and parallel component, respectively, of the wave vector of the incident beam in the crystal, $\mathbf{k}_0$:

$$\mathbf{k}_0=\mathbf{k}_{z0}-\mathbf{T} \quad \text{and} \quad k_0^2=k_0^2+v_0.$$

Then, applying the kinematical theory to the surface layer, we find that the amplitude of a superlattice reflection **s** is given by

$$u_s=i\sum_g F_{s-g}u_g, \quad (4)$$

where F_s is the structure factor of the reflection **s**.

Normal and anomalous absorption effects are neglected since the thickness of crystals used is typically less than 30 nm. Analytical expressions of the superlattice reflections are derived below for two particular cases : (*a*) normal incidence and (*b*) the two-beam case.

3. Intensity and phase of the superlattice reflections

3.1. *Normal incidence*

Superlattice reflection intensities are analytically derived here in order to be compared with the results in the case of an Si(111) crystal with 7×7 reconstruction on the bottom surface. Since six {220} reflections ($\mathbf{g}_i$: $i=1$-6) are strongly excited by the normal incidence, we have to deal with seven-beam dynamical theory (Cowley, 1975; Chang, 1984).

Eigenvalues $k_z^{(j)}$ and vectors $C^{(j)}=(C_0\ C_{g1}\ C_{g2}\ C_{g3}\ C_{g4}\ C_{g5}\ C_{g6})$ (see Fig. 2) are easily derived for a crystal of sixfold symmetry: $C^{(1)}=(a\ b\ b\ b\ b\ b\ b)$, $C^{(2)}=(a'\ b'\ b'\ b'\ b'\ b'\ b')$ for $k_z^{(1)}=Y_0+Y$ and $k_z^{(2)}=Y_0-Y$, respectively, and $C^{(j)}=(0\ c_j\ c_j^2\ c_j^3\ c_j^4\ c_j^5\ c_j^6)$ for $j=3$-7, where $c_j=\exp[i(\pi/3)j]$.

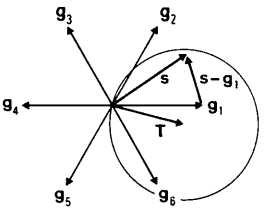

Fig. 2. Geometry of the TED spots. The reflections, $\mathbf{g}_i$ ($i=1$-6), are the Bragg reflections from {220} planes and the reflection **s** is a superlattice reflection from the surface layer. **T** is the surface-parallel component of the incident wave vector, $\mathbf{k}_0$; $\mathbf{k}_0=\mathbf{k}_{z0}-\mathbf{T}$. The circle is the section of the Ewald sphere at the 0th Laue zone.

After a short calculation starting from (3), it is derived that $Y_0=V'$ and $Y=(V^2+V'^2)^{1/2}$ for $V'=U_{g1}+U_{g1+g2}+U_{2g1}/2-\mathbf{g}_1^2/2$; $V=6^{1/2}U_{g1}$ and $(a\ b)=(\cos\alpha\ \sin\alpha/6^{1/2})$ and $(a'\ b')=(-\sin\alpha\ \cos\alpha/6^{1/2})$, where $\cos 2\alpha=-V'/Y$ and $\sin 2\alpha=V/Y$. Putting these values into (2) and (4), we find

$$u_s=i\exp(iY_0z)[F_s\cos Yz+iF_s'\sin(Yz)], \quad (5)$$

where

$$F_s'=F_s\cos 2\alpha+\left(\sum_{g=g_i}F_{s-g}/6^{1/2}\right)\sin 2\alpha. \quad (6)$$

The intensity of the superlattice reflection $I_s=|u_s|^2$ oscillates with the crystal thickness with period equal to the extinction distance, $\xi=1/2Y$, because of the interbranch interference of the Bloch waves. The superlattice reflection intensity deviates from the kinematical value $|F_s|^2$ in a simple way,

$$I_s/|F_s|^2=1+[D(\mathbf{s})^2-1](\sin Yz)^2, \quad (7)$$

depending on the deviation factor, defined by

$$D(\mathbf{s})=F_s'/F_s. \quad (8)$$

We consider here two special surface structures, (*a*) the substitutional type where atoms in the surface layer locate at the bulk lattice position, and (*b*) the displacive type where atoms are greatly displaced from the bulk lattice position. We consider first the substitutional case and assume that the surface layer contains atoms of one kind. Then, F_s and F_{s-g} have the same sign irrespective of the choice of the origin of the surface unit cell, since $\exp(i\mathbf{s}\cdot\mathbf{x})=\exp[i(\mathbf{s}-\mathbf{g})\cdot\mathbf{x}]$. Then, if $\cos 2\alpha$ and $\sin 2\alpha$ have the same sign (negative V'), from (6), (7) and (8) we find that $D(\mathbf{s})^2>(\cos 2\alpha)^2$, so that $I_s/|F_s|^2$ is larger than $1-(\sin 2\alpha)^2/2$ [we assume here $(\sin Yz)^2=\frac{1}{2}$, since TED intensities are obtained as an average over a sample area with thickness gradients]. In the case of an Si(111) crystal, we expect $I_s/|F_s|^2>0{\cdot}8$ for any superlattice reflection.* For the displacive type, on the other hand, extinction of I_s may occur when F_s and F_{s-g} have different signs.

The intensity ratios $I_s/|F_s|^2$ have been calculated for DAS structure of the Si(111) 7×7 reconstructed surface and compared with the TED experiment of the Si(111) 7×7 structure. Calculated values of F_s and F_s' and $D(\mathbf{s})$ are given in Table 1 for several reflections. Since the DAS structure is of the substitutional type (the surface atoms are located at the 1×1 lattice sites except dimer atoms), the calculated $D(\mathbf{s})$ values are larger than $\cos 2\alpha=0{\cdot}777$ as expected from

* For $\mathbf{g}_i=\{220\}$ reflection of the bulk Si crystal, $U_{g1}=4{\cdot}36$, $U_{g1+g2}=2{\cdot}03$ and $U_{2g1}=1{\cdot}66$ eV (Radi, 1970), so that $Y_0=-13{\cdot}2$ and $Y=17{\cdot}0$ eV. The period of oscillation of the intensity with thickness, the extinction distance corresponding to $1/Y$, is 24 nm, and the values of $\cos 2\alpha$ and $\sin 2\alpha$ are calculated to be 0·777 and 0·630, respectively.

Table 1. *Dynamical effect on the superlattice reflection,* $\mathbf{s}=(h\,k)$, *of the* Si(111) 7×7 *reconstructed surface*

h	k	F_s	F'_s	$D(\mathbf{s})$	$(D^2+1)/2$	I_d/I_k
3/7	0	0·390	0·507	1·30	1·31	1·00
3/7	1/7	0·157	0·242	1·54	1·68	1·37
3/7	3/7	0·0437	0·165	3·78	7·64	3·25
4/7	4/7	0·207	0·271	1·31	1·36	1·09
4/7	0	0·135	0·354	2·62	3·93	20·16
5/7	0	0·140	0·308	2·20	2·92	5·98
6/7	0	0·284	0·532	1·87	2·25	2·10
8/7	0	0·253	0·389	1·54	1·68	1·48
9/7	0	0·0986	0·146	1·48	1·54	0·87
6/7	1/7	0·244	0·394	1·61	1·80	1·69
1	1/7	0·319	0·546	1·71	1·96	1·79
1	2/7	0·202	0·341	1·69	1·93	1·89
1	3/7	0·296	0·456	1·54	1·68	1·68

Structure factors, F_s, are of the DAS structure in Takayanagi, Tanishiro, S. Takahashi & M. Takahashi (1985). $D(\mathbf{s})=F'_s/F_s$ in equation (8). I_d and I_k are the observed intensities at normal and tilted beam incidence, respectively, in Takayanagi, Tanishiro, S. Takahashi & M. Takahashi (1985). Note that the I_d/I_k are larger than 0·8.

the above theory. To evaluate values of $I_s/|F_s|^2$ from experiment, we regard the observed intensities at the normal beam incidence (I_d) as I_s and those at the tilted beam incidence (I_k), as F_s^2. Since the I_d and I_s were measured relatively [see Table I of Takayanagi, Tanishiro, S. Takahashi & M. Takahashi (1985)], we normalize them by the ratio of the calculated intensities of I_s and F_s^2 of the (1 3/7) reflection. The ratio, which is given by $(D^2+1)/2$ after averaging over thickness gradients, is evaluated to be 1·68, as shown in Table 1.* The values of I_d/I_k thus obtained, as given in Table 1, are larger than 0·8.

Dynamical intensity I_s is, thus, useful to judge whether the surface structure is of the substitutional or displacive type.

3.2. *Two-beam case*

In the case where one Bragg reflection, $\mathbf{g}=(220)$, is strongly excited in the crystal, the two-beam case may be applied. The superlattice reflection, u_s, is given by (4). Using a parameter $W=V'/V$, with $V'=\mathbf{T}\cdot\mathbf{g}-\mathbf{g}^2/2$ and $V=U_g$, u_s is expressed as

$$u_s = i\exp(iY_0z)\{F_s\cos Yz + i(1+W^2)^{-1/2}[F_{s-g}-F_sW]\sin Yz\}. \quad (9)$$

I_s/F_s^2 is given by (7) with $D(\mathbf{s})=(1+W^2)^{-1/2}(F_{s-g}/F_s-W)$. In Fig. 3, the value of $D(\mathbf{s})^2-1$ is shown as a function of W for several values of F_{s-g}/F_s.

For $W\gg1$ (the kinematical condition for the bulk crystal), superlattice reflections can have kinematical values.

For $W\lesssim1$ (the dynamical condition for the bulk crystal), $D(\mathbf{s})^2-1$ has the minimum value -1 at $W_m=F_{s-g}/F_s$. Then, according to (7), the intensity $I_s/|F_s|^2$ varies between 0 and 1 depending on the crystal thickness. Thus, at crystal thicknesses around $z=1/4Y$, I_s is reduced almost to extinction at $W_m=F_{s-g}/F_s$: W_m is positive (negative) in the case that F_s and F_{s-g} have the same (opposite) sign. $D(\mathbf{s})^2-1$ takes the maximum value of $(F_{s-g}/F_s)^2$ for $W=-F_s/F_{s-g}$, and the intensity $I_s/|F_s|^2$ varies according to (7) between 1 and $1+(F_{s-g}/F_s)^2$. Thus, at crystal thicknesses around $z=1/4Y$, we obtain the maximum value of $I_s=|F_s|^2+|F_{s-g}|^2$ for a negative (positive) W. From these criteria the relative sign of the structure factors of the surface layer can be determined. To apply the above theory to experiments, we suggest that one should observe intensity profiles with the incident beam rocking from an area with thicknesses around 1/4 or 3/4 of the extinction distance.

For $W=0$, the intensities of the superlattice reflections on the Brillouin zone boundary (BZB) ($\mathbf{s}\cdot\mathbf{g}=\mathbf{g}^2/2$) become independent of the crystal thickness, provided that the surface structure has mirror symmetry with respect to the direction of the zone boundary ($F_s=F_{s-g}$ for reflections s on the zone boundary). Therefore, the observation of TED intensities on the BZB at $W=0$ is quite useful for determining the structure factors irrespective of the crystal thickness.

4. Summary and concluding remarks

Intensities of the superlattice reflections of the reconstructed surface and/or adsorbed layer have been derived by many-beam dynamical theory for normal incidence and for the two-beam case. The theory suggests that the dynamical intensities at normal incidence are useful to discriminate between the surface layers of substitutional type and displacive type. In the two-beam case, the theory predicted that the minimum and maximum of the intensity of

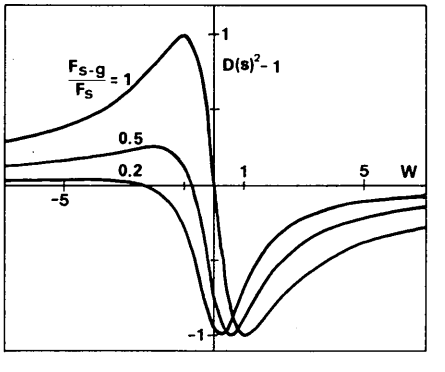

Fig. 3. Superlattice reflection intensity for the two-beam case. The variation of $D(\mathbf{s})^2-1$ with W is shown for $F_{s-g}/F_s=0·2$, 0·5 and 1. Note that the minimum value of $D(\mathbf{s})^2-1$ is -1 at $W=F_{s-g}/F_s$.

* The intensity of the (1 3/7) reflection was strong and changed less sensitively to the incident-beam direction in comparison with the other reflections.

superlattice reflections due to the incident-beam rocking are useful for determining the phases of the structure factors of the surface layer.

We proposed in a previous paper to image surface structures at atomic resolution based on a computer simulation (Takayanagi & Honjo, 1980). As seen from (5) and (6), we can obtain structure images at a special thickness of the bulk crystal, $z = 1/Y$, since the phases of the superlattice reflections depend on F_s'. It is very useful for phase determination to detect displacement of lattice fringes in high-resolution images obtained at crystal thicknesses of 1/4 and 1/2 of the extinction distance, from which we know the relative phase of F_s and F_s'.

We propose, thus, combined use of diffraction and/or high-resolution microscopy for phase determination of structure factors, in addition to kinematical intensity analyses such as those previously done for the Si(111) 7×7 reconstructed surface (Takayanagi, Tanishiro, M. Takahashi & S. Takahashi, 1985; Takayanagi, Tanishiro, S. Takahashi & M. Takahashi, 1985).

The present author expresses his sincere thanks to Dr K. Kambe for critical reading of the manuscript and discussions.

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Acta Cryst. (1990). A**46**, 86-94

Monte Carlo Calculation of A_3B (111) Ordering Transition and Surface X-ray Intensities

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(*Received* 29 *March* 1989; *accepted* 30 *August* 1989)

Abstract

A Monte Carlo simulation of an ordering phase transition in the surface region of a f.c.c.-type A_3B binary alloy is reported. The main emphasis of this simulation is the evaluation of short and long-range-order correlations near the surface which are used for calculating X-ray intensities under grazing-incident-angle conditions. These calculations suggest effective ways of conducting surface diffraction experiments on order–disorder phase transitions. The simulation results are also compared with available experimental data.

I. Introduction

The effect of the surface when a system undergoes a bulk first-order phase transition has been studied recently in much detail by various theoretical methods, including mean-field approximation (Lipowsky & Speth, 1983; Lipowsky, 1984), Landau free-energy expansion (Mejia-Lira, Benneman & Moran-Lopez, 1985), and cluster variation for semi-infinite systems (Sanchez & Moran-Lopez, 1985). The thick-film case was examined by use of a continuous Landau free-energy expansion (Lipowsky & Gompper, 1984; Sornette, 1985), and the thin-film case in the Bragg–Williams approximation (Sanchez, Mejia-Lira & Moran-Lopez, 1986). These calculations were carried out for both magnetic and binary alloy systems and focused on the order-parameter profiles in the vicinity of the phase transition. This previous work encouraged us to investigate surface effects on the order–disorder transition of A_3B-type alloys by using Monte Carlo (MC) simulation methods. MC simulations of the bulk phase transition have been carried out in the past by Golosov & Dudka (1973) and by Polgreen (1985). More recently MC simulations of three-dimensional systems including surface effects (Gompper & Kroll, 1988) have emerged.

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0108-7673/90/020086-09$03.00