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Temperature Dependence of Intensities from Silicon with Glancing Incidence HEED*

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Peak reflectivity for the 2nd to 7th order Bragg reflections of the *hhh* systematic set have been obtained at different temperatures. The results have been interpreted using an *n*-beam dynamical theory adapted to the Bragg case at glancing incidence. On the basis of this analysis it is concluded that the component of the mean-square vibrational amplitude of the surface atoms normal to the surface is about 40% greater than that of the bulk.

Considerable interest has developed in the past few years in thermal vibrations of atoms at crystal surfaces. Lattice dynamics calculations predict mean-square amplitudes which are two to three times greater than the bulk values for f.c.c. structures (see, for instance, Allen & DeWette, 1969; Wallis, Clark, Herman & Gazis, 1969).§ Such theoretical predictions have been qualitatively confirmed, for example, in the case of silver (Jones, McKinney & Webb, 1969) and copper (Woodruff & Seah, 1970; Reid, 1970), using Low-Energy Electron Diffraction (LEED). It is well known that low-energy electrons (30–500 eV) interact very strongly with the crystal lattice, and due to their low penetration, many Bragg reflections are excited simultaneously. Since the average dimensions of the coherent crystal domains are much greater than the extinction length of low-energy electrons ($\simeq$ a few Å), the diffraction process takes place in a perfect crystal region. Therefore dynamical diffraction calculations must be made to interpret the diffraction pattern. Furthermore the plane wave expansions used for high energy electrons ($E \approx 50$ KeV) do not apply, and a very involved theory has to be concocted to describe experimental results. For the simple reason that no alternative was present, much of the experimental work with respect to thermal vibrations has used in its interpretation the kinematic theory of diffraction. However, there is no *a priori* basis for this kinematic theory, although the results of measurements were not out of line with what one would expect for thermal vibrations from the surface. But it is to be stressed that there is at the present time no theoretical basis for the application of the kinematic theory. In fact, many arguments indicate that the lower-energy electron diffraction case is very far removed from those conditions that describe kinematic diffraction.

It is well known that the Bethe form of the dynamical theory of electron diffraction has been applied successfully to diffraction contrast in transmission electron microscopy and this theory should be equally valid for the energy range ($E \approx 50$ KeV) of our experiments. Using this approach several *n*-beam calculations have given successful agreement with experiment. In the present experiment these same high-energy electrons are now diffracted from a crystal in glancing angle reflection. The limited depth of penetration due to the low glancing angle gives a diffraction pattern which is sensitive to surface layers very much in the same way that the LEED pattern is sensitive to the surface. In a series of papers (Menadue, 1972; Colella, 1972; Colella & Menadue, 1972) the theory and experimental details of measurements on single crystals of silicon in ultra-high vacuum have been presented along with comparisons between absolute measured intensities and *n*-beam calculations.* The agreement between theory and experiment is reasonable except for low-order reflections, for which the roughness of the surface plays a relatively more important role. If surface roughness is the main reason for these discrepancies, the temperature dependence should not be appreciably affected. We feel that measurements of the temperature dependence and its relationship to surface vibrational amplitudes can be better determined in high-energy electron diffraction than heretofore possible in LEED experiments.

It is the purpose of this paper to discuss and compare the measured temperature dependence of the diffraction pattern of the 111 series of reflections from

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§ A recent calculation has been published on diamond structure crystals: Theeten & Dobrzynski (1972).

* Similar calculations have been recently performed by Moon & Cowley (1972) using a similar approach based on the Hill's determinant method. Their results are in qualitative agreement with ours.

silicon with theoretical predictions and to draw some conclusions as to the nature of the surface vibrational amplitudes. The details of the experimental measurements are given elsewhere (Menadue, 1972). The 222 to the 777 reflections have been measured as a function of temperature up to 600°C. In all cases the peak reflectivity was measured. Fig. 1 shows the temperature dependence of the peak intensities and is a repeat of the corresponding data in Menadue's (1972) paper. The comparison with theory is made with the formulation described by Colella (1972) and Colella & Menadue (1972). We assume a bulk Debye temperature of 543°K as determined from X-ray diffraction by Batterman & Chipman (1962). Each Fourier component of the potential V_g is modified by a Debye–Waller factor $\exp(-M)$, $M=B(\sin\theta/\lambda)^2$, which represents the formal inclusion of thermal motion in the *n*-beam dynamical theory (Ohtsuki, 1966). The crystal is assumed semi-infinite and with the bulk structure right up to the surface. The calculation is made for a number of beams sufficient that inclusion of higher-order systematic reflections will not change the calculations substantially, as checked in a few cases. Non-systematic reflections have not been considered, since the experimental conditions were chosen in such a way that their effects turned out to be negligible (Colella & Menadue, 1972). The temperature dependence of the intensity is obtained by calculating the reflectivity at each temperature and then taking the slope of the logarithmic intensity *versus* temperature plot. The calculations show that all the semi-logarithmic plots are approximately linear, as observed experimentally. The calculated temperature dependence of the intensity will be, in general, steeper than the two-beam value with the same Debye parameter, since higher order reflections are involved. For the calculations, the ratio V_g'/V_g between complex and real parts of the Fourier coefficients of the potential was taken as 0·1. A discussion and justification for this value is given elsewhere (Colella & Menadue, 1972). We present in Table 1 (second column) the experimental slopes determined from data such as those in Fig. 1 and the slopes determined from the temperature dependences of the calculated *n*-beam systematic reflections as a function of temperature (3rd and 4th columns). The 222 reflection, which in our calculation has zero structure factor, is present as one of the strongest reflections and this is entirely due to systematic reflections of the allowed structure factors: 111, $\overline{1}\overline{1}\overline{1}$, 333, 444. However, for this reflection, the comparison between theory and experiment is worst (see Colella & Menadue, 1972, and Moon & Cowley, 1972). This is probably due to the fact that the surface conditions play an important role at a very small angle of incidence. Neglecting the 222 reflection, it can be seen (2nd and 3rd column) that the experimental slopes range from a factor of about 2 times greater than the calculation for the 333 to roughly 30% greater for the 777 reflection. The fifth column in Table 1 gives a parameter related to the depth of pentration of the wave field for the different reflections. This is the depth at which the total wave field in the *n*-beam calculation has dropped to $1/e$ of its initial intensity and hence is a measure of the depth of the surface sampled by the beam for that particular reflection. The next column gives the depths of penetration in terms of layers. It can be seen that the depth ranges from approximately 2 layers for the 333 to 7 layers for the 777. A layer in this case is defined as the close-spaced (111) double layer and a layer spacing corresponds to the separation of such (111) double layers. Thus one would expect that the temperature dependence of the 777 reflection

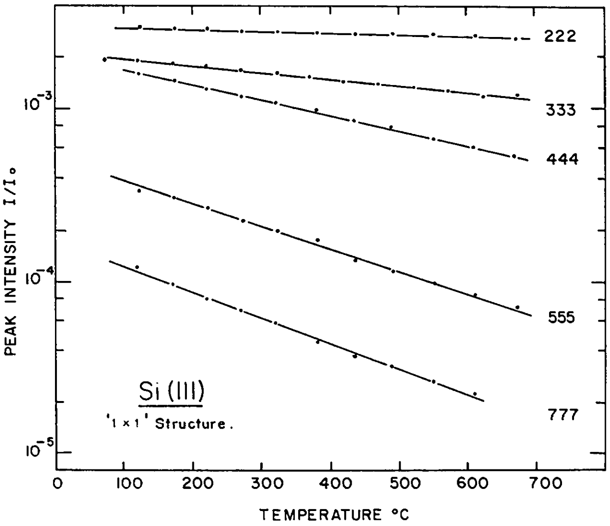

Fig. 1. Semi-log plot of peak intensities as a function of temperature for the *hhh* systematics of silicon.

Table 1. *Experimental and n-beam calculated slopes for the hhh systematics of silicon*

The slopes are expressed as: d log $(I_{\max}/I_0)/\mathrm{d}T$. (decade/K°). B is the Debye parameter: $8\pi^2\bar{u}^2_{111}$.

hkl	Peak-slope experimental ($\times 10^{-4}$)	Peak-slope calculated $B=B_{\text{bulk}}$ ($\times 10^{-4}$)	Peak-slope calculated $B=1\cdot4\ B_{\text{bulk}}$ ($\times 10^{-4}$)	Extinction length Å	Layer penetration
222	1·88±0·62	0·244	0·344	3·3	1·1
333	4·83±0·57	2·41	3·55	7·1	2·3
444	8·46±1·0	4·74	6·85	11	3·5
555	14·8±1·3	8·62	12·4	16	5·1
777	20·9±2·0	15·6	22·3	23	7·4

should be more representative of that of the bulk than the 333.

The question that now arises is how do we make an intelligent comparison of this difference between the temperature dependence calculated for a semi-infinite perfect crystal and the actual measured data in terms of the effective vibrational amplitude of the surface atoms. One means of accomplishing this comparison is to find empirically the value of the Debye–Waller factor $\exp(-M)$ that gives the best fit to all the temperature dependent data. When one replaces the Fourier potential term $V_g.\exp(-M)$ by $V_g.\exp(-1{\cdot}4M)$, determined by trial and error, and computes all the intensities as a function of temperature and then determines the slope for each reflection *hhh*, the data is presented in column 4 of Table 1. The slope determined in this empirical way can be seen to be in reasonable agreement with the experimentally determined temperature dependence. Upon this interpretation and realizing that M is proportional to the mean-square amplitude of vibration normal to the (111) planes one would conclude that the average surface atom has a mean-square amplitude some 40% bigger than that known to exist for the bulk atoms. Although the assumption we have used implies that all the atoms (surface and bulk) have an increased amplitude, it probably does not alter the results strongly since the first few layers will make the major contribution to the intensity. In any event the 40% figure is a weighted average for the first few layers. The same result has been obtained independently for Si(111) by means of LEED (Nesterenko & Borodkin, 1971).*

It can be noted at this point that the same experimental data of Table 1 can be reasonably well fitted by a kinematic dependence $\exp(-2{\cdot}8M)$, which corresponds to a mean square amplitude 1·4 bigger than the bulk value. It appears, therefore that the same conclusion would have been reached by a two-beam kinematic approach applied to the temperature dependence of the peak values. However, there is no theoretical basis for this approach, because the diffraction process is intrinsically *n*-beam dynamic, as proved by the strong 222 intensity. This coincidence is probably a fortuitous effect. When a particular *hkl* reflection is considered as a function of temperature, the presence of other high-order simultaneous reflections will produce a steeper temperature dependence. It so happens, in many cases, that its value turns out to be very close to that of a two-beam kinematic dependence, $\exp(-2M_{\text{surf}})$. Given the order of magnitude of the uncertainties involved, both in theory and experiment, we feel that no particular significance can be attached to this coincidence at this time.

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* Theeten & Dobrzynski's (1972) calculations predict a much higher value for the mean square displacement normal to the (111) surface of silicon (3·7 times the bulk value). Their calculations, however, are valid for atoms right at the surface.

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