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The Measurement of Inner Potential for Diamond, Germanium and Silicon

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Abstract

Measurements of the inner potentials for diamond, germanium and silicon have been made using the Shinohara method and Kikuchi lines. In the case of germanium, a method has been derived which allows the use of crystals appreciably off-cut from nominal {*hkl*} artificially prepared faces. The mean values obtained are 18·2 V for diamond, 13·4 V for germanium and 10·9 V for silicon. Comparisons are made with previous experimental results and theoretical calculations.

Introduction

In a previous account of the measurement of the inner potential of diamond (Goswami & Lisgarten, 1980) three crystals were examined. One of these had a natural {111} face, the other two having artificially polished {100} and {111} faces respectively. Of those results using the Shinohara (1932) method, a value of 17·3 ± 1·5 V was obtained for the {111} natural-faced diamond, compared with 13·2 ± 1·7 V for a crystal having an artificially prepared {111} face. Hartmann, Niemitz & Schwarzer (1975), using a (basically) similar method, obtained 18·6 ± 2·2 V. The reason for the comparatively low value of 13·2 ± 1·7 V is not clear, but some subsequent experiments carried out on crystals of germanium which had artificially prepared {100} faces (but off-cut by 1·2° from the true {100} plane) showed that, unless a revised method was used to measure the inner potential, manifestly low values could be obtained if the normal Shinohara process was employed. It is therefore possible that the diamond having the artificially prepared {111} face might also have been off-cut by about 1°; this unfortunately cannot now be confirmed as this crystal is no longer available. In view of this and the fair agreement between the Hartmann *et al.* (1975) value and the value for the above crystal with the natural {111} face, a further investigation has been carried out on this diamond, again using the Shinohara method.

At the same time the present work has been extended to include measurements for the inner potential of silicon and germanium using Kikuchi lines parallel to the shadow edge for specimens examined in the reflection position with high-energy (~40 kV) electrons. The revised method mentioned above is described in the next section and is used to interpret the photographic records obtained from the off-cut germanium crystals.

Method

The Shinohara method using Kikuchi lines parallel to the shadow edge has been used for the diamond, silicon and two cleaved {111} germanium crystal specimens. The details of this method have already been given in some detail in a previous paper (Goswami & Lisgarten, 1980). Two additional specimens of germanium single crystals had prepared {100} (nominal) faces, but were off-cut by about 1·2°. For the crystals positioned in the camera as shown in Fig. 1, four Kikuchi lines (16th, 12th, 8th and 4th orders) were clearly visible, but, because of the off-cut, the Shinohara method could not be used. Nevertheless, if the following procedure is carried out, off-cut crystals can be used.

The camera length, L (the photographic plate-to-crystal specimen distance), and a series of calculations using wavelengths, λ_0, from 0·0575 to 0·0585 Å for assumed inner potential values, Φ, from 12 to 15 V are used to obtain *calculated* values for the distances of the 8th-, 12th- and 16th-order Kikuchi lines from the central spot. (The 4th order is ignored because the broadness of this line does not allow sufficiently accurate *experimental* measurements to be

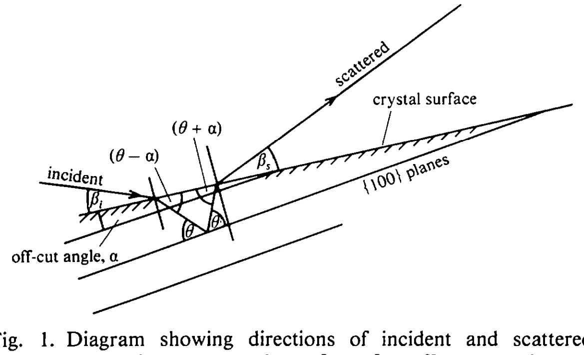

Fig. 1. Diagram showing directions of incident and scattered electrons with respect to the surface of an off-cut crystal.

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made.) The 16th-order Kikuchi line is taken to be coincident with the 16th-order Bragg spot in all cases.

For a given wavelength, λ_0, angle of off-cut α, and assumed inner potential value Φ, it can readily be shown (see Fig. 1) that the glancing angle of incidence, β_i, made by the electron beam with the crystal surface is given by

$$\sin^2\beta_i = 1 - \mu^2\{1 - \sin^2(\theta - \alpha)\} \quad (1)$$

and the corresponding angle of reflection of scatter, β_s, is given by

$$\sin^2\beta_s = 1 - \mu^2\{1 - \sin^2(\theta + \alpha)\}, \quad (2)$$

where μ, the refractive index, is given by

$$\mu^2 = 1 + \frac{\Phi}{P} = \frac{\lambda_0^2}{\lambda_i^2}, \quad (3)$$

λ_0 being the wavelength of the electrons *in vacuo* corresponding to the accelerating potential, P, and λ_i, the wavelength inside the crystal. The Bragg angle θ, inside the crystal, is given by

$$2d \sin\theta = n\lambda_i, \quad (4)$$

where d is the crystal-plane spacing ($\{100\}$ in this case) and n is the Bragg-reflection order number.

The calculated distances of the 16th-order Bragg spot/Kikuchi line from the central spot are determined using the appropriate values of β_i and β_s obtained from (1) and (2) for given values of λ_0 and α. The calculated distances of other orders (12th and 8th in the present case) are obtained using β_i for the 16th order with the appropriate β'_n as defined by the equation below. Calling these distances r'_{16}, r'_{12}, r'_8, the following values of β'_n can be found thus:

$$\beta'_{16} = \tfrac{1}{2}\tan^{-1} r'_{16}/L$$
$$\beta'_{12} = \tan^{-1} r'_{12}/L - \tfrac{1}{2}\tan^{-1} r_{16}/L$$
$$\beta'_8 = \tan^{-1} r'_8/L - \tfrac{1}{2}\tan^{-1} r_{16}/L$$

(see Goswami & Lisgarten, 1980).

(Note β'_{16}, β'_{12} and β'_8 should not be confused with true angles of scatter β for Kikuchi lines as $\beta_i \neq \beta_s$ if crystal is off-cut.) Values of $\sin^2\beta'_n$ are subtracted from corresponding values of $n^2\lambda_0^2/4d^2$, the difference being compared with similar calculations for zero off-cut angle (*i.e.* true values of $\mu^2 - 1$ for wavelength λ_0). The ratio of the difference for $\alpha = 0$ to the difference for an off-cut angle α gives a correction factor, F. It has been found, for a given value of α, F is very nearly independent of λ_0 and Φ for the ranges already indicated. Fig. 2, which shows a graph of F against α for the 8th-, 12th- and 16th-order Kikuchi lines, summarizes the complete calculation. λ_0 is found directly by means of a polycrystalline-thin-film preparation of aluminium which is placed in the path of the electron beam after the germanium crystal has been withdrawn. Thus

$$\mu^2 - 1 = F[n^2(\lambda_0^2/4d^2) - \sin\beta'_n]. \quad (5)$$

{A more direct calculation based on the total deviation $(\beta_i + \beta_s) = \psi$ for the 16th-order Bragg spot/Kikuchi line can be made using (1) and (2), *i.e.*

$$\psi = \cos^{-1}[(\mu^2 - k^2)^{1/2}\cos\alpha + k\sin\alpha] + \cos^{-1}[(\mu^2 - k^2)^{1/2}\cos\alpha - k\sin\alpha],$$

where $k = 16\lambda_0/2d$ for the 16th order; this can be solved iteratively for μ^2. The complete calculation, however, using the 8th and 12th orders, is lengthy and requires considerable computational accuracy.}

The inner potential Φ is evaluated using (5) in

$$\Phi = \frac{(\mu^2 - 1)h^2}{2em_o\lambda_0^2}\left(1 + \frac{h^2}{m_0^2e^2\lambda_0^2}\right)^{-1/2},$$

where h is Planck's constant, e is the electron charge, m_0 is the electron rest mass and c is the velocity of light.

Experimental

All specimens were examined in the reflection mode in a vertical electron diffraction camera. In the present work a marker indicating the precise position of the centre of the specimen chamber was used to ensure that the position of each crystal with respect to the electron beam remained the same and that the axis of rotation (angle of incidence) lay in the surface of the crystal;

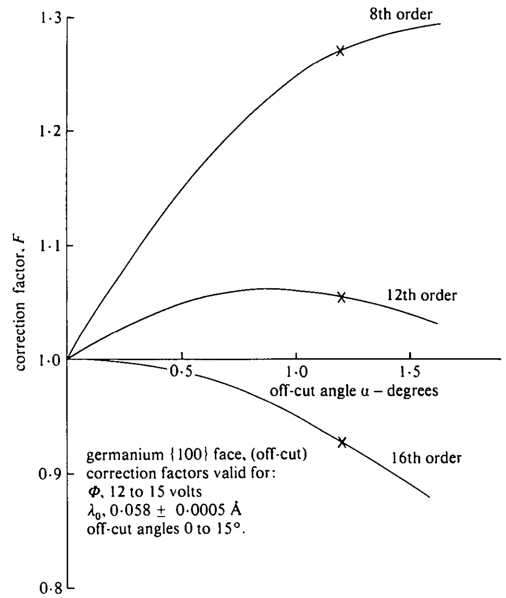

Fig. 2. Graph showing variation of correction factor, F, with angle of off-cut, α. F is the ratio of the true to the apparent value of the inner potential for a given order number of Kikuchi lines parallel to the shadow edge.

this reduces the uncertainty in the camera length ($L = 39{\cdot}0 \pm 0{\cdot}2$ cm).

In all cases a high-order Bragg reflection spot was brought into coincidence with the corresponding Kikuchi lines parallel to the shadow edge and during the recording of the lines the undeflected beam was intercepted to prevent charging of the photographic plate. Subsequently the crystal was withdrawn and a second exposure was made, allowing the undeflected beam to mark the position of the central spot. Central spot regions on the plates were reduced chemically to render the central spots clearly visible and distances between these and the Kikuchi lines were measured using a travelling microscope.

For the off-cut-germanium-crystal experiments, λ_0 was measured to about 0·2% from the Al film.

Results

All of the inner potential values have been obtained using Kikuchi lines parallel to the shadow edge, as indicated in the section of experimental procedure. These are summarized in Table 1 and illustrated by the histograms of Fig. 3.

Table 1. *Inner potential for several specimens*

Crystal	Method	Inner potential (V) average values
Diamond {111} cleavage face	Shinohara	18·2 ± 0·5
Silicon {100} prepared face	Shinohara	11·0 ± 0·7
Silicon {111} prepared face	Shinohara	10·7 ± 0·7
Germanium {111} cleavage face	Shinohara	13·5 ± 0·5 (based on 8 measurements)
Germanium {100} prepared face, 1·2° off-cut	Correction factor (see § 2)	13·3 ± 1·2

Comments and summary

All of the inner potential investigations in the present work have been carried out using the Shinohara method and the Kikuchi lines which are parallel to the shadow edge. (In the case of the off-cut germanium crystal a modified procedure using these Kikuchi lines has been described.) It is thought that the above methods are likely to be more accurate than that of Yamaguti (1930, 1932) as the measurements using lines are generally more precise than those involving a number of Bragg reflection spots. Furthermore, the recording of the lines is simpler than that for Bragg spots since a simple exposure is sufficient to photograph all of the lines simultaneously with the crystal in a fixed position.

Diamond

In the light of the present work it is necessary to reconsider some remarks made by Goswami & Lisgarten (1980). It is now believed that the value of 18·2 ± 0·5 V is the best so far obtained (see histogram of Fig. 3), and this agrees very well with the value of 18·6 ± 2·2 V obtained by Hartmann *et al.* (1975). The value obtained by Goswami & Lisgarten is a little lower at 17·3 ± 1·5 V, but the difference is not significant; the present work, however, claims a generally higher accuracy. As already mentioned, the significantly lower values obtained previously, where the Shinohara method had been employed, could be explained if the diamond with an artificially prepared face were off-cut. What remains unexplained is the previous Yamaguti (1930, 1932) method result of 15·2 ± 1·9 V for the diamond with a natural {111} face [although many of the individual results were appreciably greater than the average – see Goswami & Lisgarten (1980)]. This, it is hoped, will be investigated later.

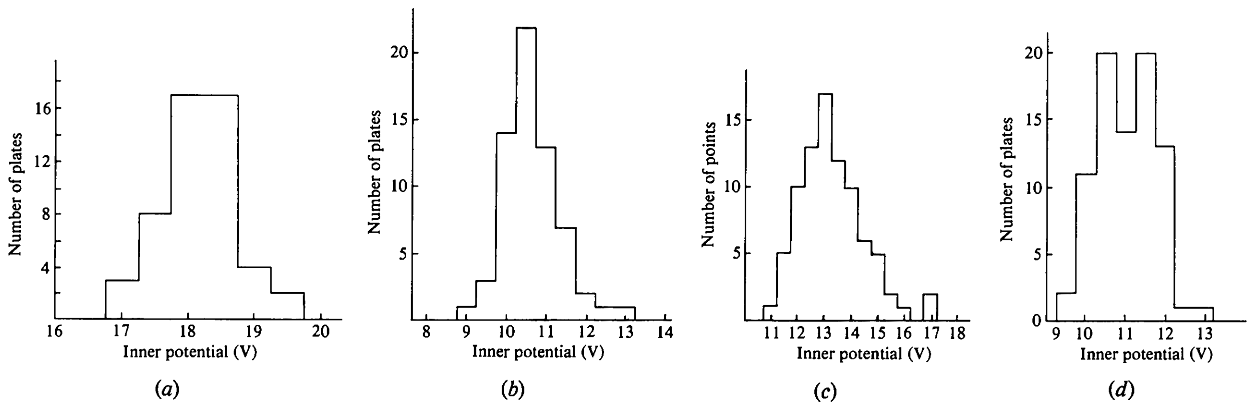

Fig. 3. Histograms of measurements for (*a*) diamond {111} face, (*b*) germanium {100} (nominal) face, (*c*) silicon {111} face, (*d*) silicon {100} face. For diamond, silicon and cleaved germanium crystals (single specimens of diamond and germanium and several different specimens of silicon), photographic plates were exposed for random azimuthal settings. In the case of the two off-cut germanium crystals several plates were exposed for a single azimuth (consistent with Fig. 1) and here the ordinates refer to individual values based on each Kikuchi line measured. The ordinates in all other cases refer to the number of plates since one value is associated with each plate.

Silicon

All of the crystals examined had artificially prepared faces but off-cutting was not detected. The values obtained, 11.0 ± 0.7 and 10·7 ± 0·7 V for {100} and {111} faces, respectively, are in good agreement. Gaukler & Schwarzer (1971), using Kikuchi lines parallel to the shadow edge, obtained 11·5 ± 1·0 V for {111} crystal faces. These workers considered the effect of off-cut faces and their result is quoted for a crystal with an off-cut angle lying between 0·1 and 0·15°.

The somewhat higher value of 12 ± 0·4 V obtained by Menadue (1970) was based on the assessment of the angular positions of Bragg spots and a separately measured wavelength. A similar value of 12·0 ± 0·05 V was obtained by Britze & Meyer-Ehmsen (1978) using 10 keV electrons and a {100} surface; it was determined from the angle of incidence for which there was a strong excitation of the 004 reflection at azimuth [130] since there was no noticeable excitation of additional reflections. Misorientation of the surface was stated to be less than 0·25°. A relatively few measurements using the Yamaguti method for a {100} surface made by Goswami & Lisgarten (1980) yielded a value of 11·8 ± 1·0 V.

Overall, the values for the inner potential of silicon obtained by the above experimenters are in fairly good agreement.

Germanium

A few measurements have been made on two crystals which had good {111} cleavage faces. These measurements, using the Shinohara method, gave 13·5 ± 0·5 V. It was not possible to obtain further good cleavage faces and experiments carried out on two off-cut crystals having, nominally, {100} faces gave a similar if rather less accurate value of 13·3 ± 1·2 V. These values compare with a result of 15·4 ± 0·8 V obtained by Hoffman & Jönsson (1965), using the electron biprism method. The reason for the difference (~2 V) between the above two values is not known.

The modified method, using the off-cut crystals, also involves setting a Bragg-reflection spot to the corresponding Kikuchi line parallel to the shadow edge, and it is possible that if the surfaces of the crystals are stepped the positions of the Bragg spot could be affected. It is known that such stepping can give rise to 'half-value' inner potentials (see, for example, Tull, 1951). To check this point shadowed replicas were made of the crystal surfaces and examined in an electron microscope. Steps were not detected, although some features due to polishing were observed; it is concluded, therefore, that the positions of Bragg spots had not been influenced.

Table 2. *Inner potentials calculated by Radi* (1970) (V)

	'High value'	'Low value'
Diamond	19·75	15·93
Germanium	13·82	13·69
Silicon	12·20	11·47

Note on errors of measurement

Overall errors have been assessed on the basis of a standard-deviation calculation, although the histograms of Fig. 3 show the extreme range of the values obtained. Random errors arise principally from visual setting in the diffraction camera. A smaller contribution to the random errors is associated with uncertainty as to the precise point of incidence of the electron beam on the face of the crystal specimen, which, in turn, leads to some uncertainty in the value of the camera length, L (about $\frac{1}{2}$%).

Theoretical values

Table 2 shows inner potentials calculated by Radi (1970). The 'high' value is based on the appropriate free atom, an approach which is probably too crude and which in the case of diamond leads almost certainly to a result which is too large. For the 'low' value Radi uses a method in which the outer four electrons are assigned a constant density over the atomic volume. This is a suitable approach for metals, but it is very unlikely to be so for diamond; it is, however, probably a reasonable one for germanium and silicon. In any case the two values given for these latter two elements are close to one another, whereas for diamond there is a difference of almost 4 V.

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