

## 5. DETERMINATION OF LATTICE PARAMETERS

pattern. Formula (5.3.3.34), since  $C'A' = R \cos \mu$ , can be presented in another form:

$$R = \frac{H^2 - H_p P}{2H_n \cos \mu \cos \beta}, \quad (5.3.3.35)$$

where two setting angles,  $\mu$  and  $\beta$ , are taken into account. When the indices are known, both (5.3.3.34) and (5.3.3.35) can be used for the determination or refinement of lattice parameters.

Another analytical method for indexing multiple-diffraction patterns, based on the determination of the Lorentz point, has been described by Kshevetsky, Mikhailyuk, Ostapovich, Polyak, Remenyuk & Fomin (1979).

Formulae (5.3.3.34) and (5.3.3.35) are valid for all crystal systems. In practice, however, the rather complicated method is used mainly for cubic crystals, and a special approach proved to be needed in order to adapt the method to other (rectangular) systems (Kshevetsky, Mikhalchenko, Stetsko & Shelud'ko, 1985). In the case of a cubic lattice, it is convenient to substitute

$$R = a/\lambda \quad (5.3.3.35a)$$

into (5.3.3.34) and (5.3.3.35) rather than  $R = 1/\lambda$  used in the general case, so that the lengths of the reciprocal vectors, being now functions of the indices only, are:

$$P = (h_0^2 + k_0^2 + l_0^2)^{1/2}, \quad (5.3.3.35b)$$

$$H = (h^2 + k^2 + l^2)^{1/2}, \quad (5.3.3.35c)$$

$$H_p P = \mathbf{HP} = h_0 h + k_0 k + l_0 l. \quad (5.3.3.35d)$$

The lengths of the components of  $\mathbf{H}$  can be determined from (5.3.3.35b,c,d) taking  $H_p = H_p P/P$  and  $H_n = (H^2 - H_p^2)^{1/2}$ . After introducing the alterations [equation (5.3.3.35a) and the resulting equations (5.3.3.35b,c,d)], (5.3.3.35) now describes a simple dependence between the ratio  $a/\lambda$ , the indices, and the setting angles.

The accuracy of the lattice-parameter determination resulting from (5.3.3.35) in the cubic case can be assumed to be:

$$\frac{\Delta a}{a} = \tan \mu \Delta \mu + \tan \beta \Delta \beta; \quad (5.3.3.36)$$

this thus depends on the values of the setting angles  $\beta$ ,  $\mu$  and their accuracies  $\Delta \beta$ ,  $\Delta \mu$ . The latter depend on various systematic errors.

Since the differences between the two angular settings at which a given set of planes diffracts are measured rather than their absolute values, the systematic errors due to absorption, specimen displacement, and zero-setting are eliminated. In contrast, errors due to vertical divergence, refraction and the change of wavelength of the incident radiation (when it enters the crystal), alignment, and dynamical effects should be taken into account. In the case described by Post (1975), when a fine focus (effective size  $0.4 \times 0.5$  mm) and collimation limiting the beam divergence to  $2'$  were used, the vertical divergence causing the relative error in  $d$  of about  $5 \times 10^{-8}$  could be ignored.

The errors due to the real structure (inhomogeneity, mosaicity and internal stress) were discussed by Kshevetsky *et al.* (1979).

The accuracy possible by this method (from 1 to 4 parts in  $10^6$ ) is comparable with that obtained with the Bond (1960) method. The advantages of this method from the point of view of lattice-parameter determination are as follows:

(a) a large number of reflections can be measured without realigning or removing the crystal;

(b) all the lattice parameters can be determined and not only one, as in the Bond (1960) method;

(c) the narrow diffraction profiles can be located with very high accuracy and precision;

(d) the arrangement makes it possible to remove some systematic errors;

(e) the high accuracy resulting from (a)–(d), which is comparable with that obtained by means of the Bond (1960) method;

(f) the high precision that results from (a) and (c).

A disadvantage, on the other hand, is the complicated interpretation (indexing) of multiple-diffraction patterns, so that this method is less popular than the Bond (1960) method.

The Post (1975) method has been applied to the accurate lattice-parameter determination of germanium, silicon, and diamond single crystals (Hom, Kiszénick & Post, 1975).

## 5.3.3.7. Multiple-crystal – pseudo-non-dispersive techniques

## 5.3.3.7.1. Double-crystal spectrometers

Detailed information concerning the double-crystal spectrometer, which consists of two crystals successively diffracting the X-rays, can be found in James (1967, pp. 306–318), Compton & Allison (1935), and Azároff (1974). This device, usually used for wavelength determination, may also be applied to lattice-parameter determination, if the wavelength is accurately known. The principle of the device is shown in Fig. 5.3.3.8. The first crystal, the monochromator, diffracts the primary beam in the direction defined by the Bragg law for a given set of planes, so that the resulting beam is narrow and parallel. It can thus be considered to be both a collimator (or an additional collimator, if the primary beam has already been collimated) and a wavelength filter. The final profile  $h(\theta)$ , obtained as a result of the second diffraction by the specimen when the first crystal remains stationary and the second is rotated, is narrower than that which would be obtained with only one crystal. The final crystal profile  $h_c(\theta)$  [cf. equation (5.3.1.6)] is due to both crystals, which, if it is assumed that they are cut from the same block, can be described by the autocorrelation function (Hart, 1981):

$$h_c(\theta) = K \int_{-\infty}^{\infty} R(\theta') R(\theta' - \theta) d\theta', \quad (5.3.3.37)$$

where  $R(\theta)$  is an individual reflectivity function of one crystal and  $K$  is a coefficient of proportionality. Its half-width is 1.4 times larger than that related to only one crystal. In spite of this, the recorded profile can be as narrow as, for example,  $2.6''$  (Godwod, Kowalczyk & Szmíd, 1974), since the profile due to the wavelength  $h_i(\theta)$ , modified by the first crystal, is extremely narrow. Additional advantages of the diffraction profile are: its symmetry, because  $h_c(\theta)$  is symmetric as an effect of autocorrelation, and smoothness, as an effect of additional integration. The profile can thus be located with very high accuracy and precision.

When there is a small difference in the two lattice spacings, so that one has a value  $d$  and the other  $d + \delta d$ , if  $\delta \lambda / \lambda$  is small enough, it can be assumed that the profile does not alter in shape but in its peak position [cf. §5.3.3.4.3.3, paragraph (3)]. If for two identical crystals this were located at  $\theta_0$ , the peak position

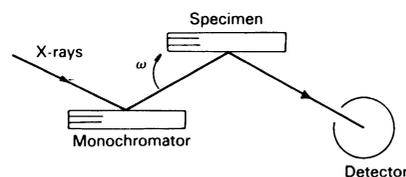


Fig. 5.3.3.8. Schematic representation of the double-crystal spectrometer.

### 5.3. X-RAY DIFFRACTION METHODS: SINGLE CRYSTAL

shifts to  $\theta_0 - \tan \theta \delta d/d$ . The measurement of this shift rather than the absolute position of the rocking curve is the basis of all the double-crystal methods. An example of the application of a double-crystal spectrometer with photographic recording has been given in §5.3.2.3.5 (Bearden & Henins, 1965).

The basic requirements that should be fulfilled to make the most of the double-crystal spectrometer are: limitation of the primary beam by means of a collimator, parallelism of the two axes [precision as high as  $1''$  obtained by Godwod, Kowalczyk & Szmíd (1974)], and high thermal stability (0.1 K; Godwod, Kowalczyk & Szmíd, 1974). Alignment procedure, errors, and corrections valid for the double-crystal spectrometer have been considered by Bearden & Thomsen (1971).

The double-crystal diffractometer, because of the small width of the diffraction profile, is a very suitable tool for local measurements of lattice-parameter differences, for example between an epitaxial layer and its substrate. Hart & Lloyd (1975) carried out such a measurement on a standard single-axis diffractometer (APEX) to which a simple second axis, goniometer head, and detector were added (Fig. 5.3.3.9). The diffracted beam was recorded simultaneously by three detectors. A *symmetric arrangement* with two detectors,  $D_1$  and  $D_2$ , with no layer present, makes possible the determination of the absolute value of the lattice parameter of the substrate, as in the Bond (1960) method. The third detector makes it possible to record the double-crystal rocking curve, which usually fully resolves the layer and substrate profiles. The changes in the lattice parameter between the two components can be used for determination of strain (at 1 part in  $10^4$ ).

The very important advantage of this method, from the point of view of local measurements, is that single- or double-crystal diffraction can be selected, simultaneously if needed, on exactly the same specimen area. Other examples of strain measurements by means of a double-crystal spectrometer are given by Takano & Maki (1972), who measured lattice strain due to oxygen diffusing into a silicon single crystal; by Fukahara & Takano (1977), who compared experimental rocking curves and theoretical ones computed within the frame of the dynamical theory; and Barla, Herino, Bomchil & Pfister (1984), who examined the elastic properties of silicon.

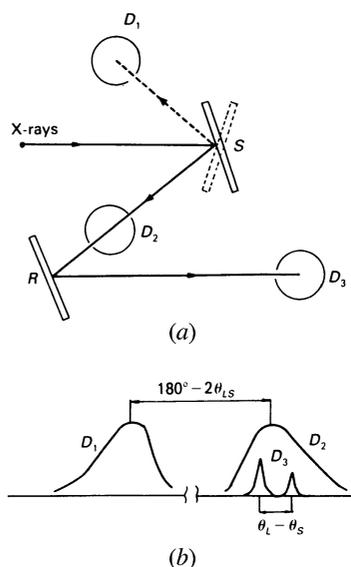


Fig. 5.3.3.9. Schematic representation of the double-crystal arrangement of Hart & Lloyd (1975) for the examination of epitaxial layers. (a) Experimental set-up. (b) Diffraction profiles recorded by detectors  $D_1$ ,  $D_2$ , and  $D_3$ .

The standard double-crystal technique does not allow determination of relatively small strains, *i.e.* ones that affect the lattice parameter by, for example, less than 2–3 parts in  $10^5$ , as in the case of (004) Si reflection and Cu  $K\alpha$  radiation. To overcome this difficulty, Zolotoyabko, Sander, Komem & Kantor (1993) propose a new method that combines double-crystal X-ray diffraction with *high-frequency ultrasonic excitation*. Since ultrasound has a wavelength a little less than the X-ray excitation length, it affects the diffraction profile close to the Bragg position and so permits the detection of very small profile broadenings caused by lattice distortions. With this method, lattice distortion as small as 5 parts in  $10^6$  can be measured.

As has been shown in the case of the device used by Hart & Lloyd (1975), the symmetric arrangement due to Bond (1960) proves to be very useful when the double-crystal spectrometer is to be used for absolute lattice-parameter determination, since such an arrangement combines the high precision and sensitivity of a double-crystal spectrometer with the high absolute accuracy of the Bond method. Other examples of a similar idea are presented by Kurbatov, Zubenko & Umansky (1972), who report measurements of the thermal expansion of silicon; Godwod, Kowalczyk & Szmíd (1974), who also discuss the theoretical basis of their arrangement; Ridou, Rousseau & Freund (1977), who examine a phase transition; Sasvári & Zsoldos (1980), and Fewster (1982). The latter two papers are concerned with epitaxial layers. A rapid method is proposed by Sasvári & Zsoldos (1980) for deconvoluting the overlapping peaks due to the layer and the substrate. A particular feature of the arrangement proposed in the first of these papers (Kurbatov, Zubenko & Umansky, 1972) is the use of a germanium-crystal monochromator with anomalous transmission, to obtain a nearly parallel primary beam (the horizontal divergence is  $28''$  and the vertical  $14''$ ).

The error analyses given by Godwod, Kowalczyk & Szmíd (1974) and Sasvári & Zsoldos (1980) show that systematic errors due to eccentricity, absorption, and zero position are eliminated experimentally, owing to the symmetric arrangement, as in the Bond (1960) method. In contrast, the errors due to crystal tilt, refraction and the Lorentz-polarization factor [their uncertainties in lattice parameters, as evaluated by Sasvári & Zsoldos (1980), are  $10^{-6}$  Å each], axial divergence ( $2 \times 10^{-6}$  Å), angle reading ( $10^{-4}$  Å), and instrument correction and calculations (each to  $5 \times 10^{-5}$  Å) should be taken into account. The effect of absorption, discussed by Kurbatov, Zubenko & Umansky (1972), proved to be negligible. The final accuracy achieved for silicon single crystals by Godwod, Kowalczyk & Szmíd (1974) is comparable with that obtained by Bond (1960).

A specific group of double-crystal arrangements is formed by those in which *white X-radiation* is used instead of characteristic. Such an arrangement makes possible very large values of the Bragg angle (larger than about  $80^\circ$ ), which increases the accuracy, precision, and sensitivity of measurement of the lattice parameters and their change with change of temperature. This task is rather difficult to realize by means of

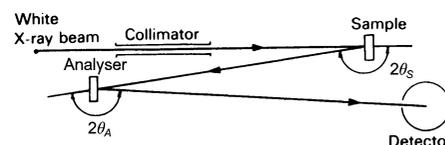


Fig. 5.3.3.10. Schematic representation of the double-crystal arrangement of Okazaki & Kawaminami (1973a); white incident X-rays are used.

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traditional methods, in which both the wavelengths and the lattice parameters are fixed, and it is difficult to find a suitable combination of their values.

The principle of the method presented by Okazaki & Kawaminami (1973a) is shown in Fig. 5.3.3.10. The first crystal (the specimen to be measured) remains fixed during a single measurement, the second (the analyser) is mounted on the goniometer of an X-ray diffractometer and can be operated with either an  $\omega$  or a  $\theta$ - $2\theta$  scan. As diffraction phenomena appear for both the specimen and the analyser (in general of different materials) whose interplanar spacings are equal to  $d_s$  and  $d_A$ , respectively, the following relation results from Bragg's law:

$$d_s \sin \theta_s = d_A \sin \theta_A, \quad (5.3.3.38)$$

where  $\theta_s$  and  $\theta_A$  are the respective Bragg angles. Since  $d_A$  and  $\theta_s$  are kept constant, a change in  $d_s$  as a function of temperature is determined from a change in  $\theta_A$ . The relative error  $\delta d/d$  resulting from (5.3.3.38) with  $\theta_A \approx 90^\circ$  is

$$\begin{aligned} \frac{\delta d_s}{d_s} &= \cot \theta_A \delta \theta_A = \tan(\pi/2 - \theta_A) \delta \theta_A \\ &\approx (\pi/2 - \theta_A) \delta \theta_A. \end{aligned} \quad (5.3.3.39)$$

The method initiated by Okazaki & Kawaminami (1973a) has been developed by Okazaki & Ohama (1979), who constructed the special diffractometer HADOX (the positions of the specimen and the analyser were interchanged) and discussed systematic errors. Precision as high as 1 part in  $10^7$  was reported. Examples of the application of such an arrangement for measuring the temperature dependence of lattice parameters were given by Okazaki & Kawaminami (1973b) and Ohama, Sakashita & Okazaki (1979). Various versions of the HADOX diffractometer are still reported. By introducing two slits (Soejima, Tomonoga, Onitsuka & Okazaki, 1991) – one to limit the area of the specimen surface to be examined and the other to define the resolution of  $2\theta$  – it is possible to combine  $\omega$  and  $2\theta$  scans and obtain a two-dimensional intensity distribution in the plane parallel to the plane of the diffractometer, and to determine the temperature dependence of lattice parameters on a selected area of the specimen (avoiding the effects of the surroundings). The HADOX diffractometer may work with both a rotating-anode high-power X-ray source (examples reported above) and a sealed-tube X-ray source. In the latter case (Irie, Koshiji & Okazaki, 1989), to increase the efficiency of the X-ray tube, the distance between the X-ray source and the first crystal has been shortened by a factor of five. As is implied by (5.3.3.39), one can increase the relative precision of the method by using the analyser angle close to  $\pi/2$ . This idea has been realized by Okazaki & Soejima (2001), who achieved the relative accuracy of determination of lattice-parameter changes as high as 1 part in  $10^9$ – $10^{10}$  by extending the Bragg angle from  $78^\circ$  (previous versions) to  $89.99^\circ$  and by elimination of systematic errors due to crystal tilt, crystal displacement, temperature effects and radiation damage.

An original method for the measurement of lateral lattice-parameter variation by means of a double-crystal arrangement

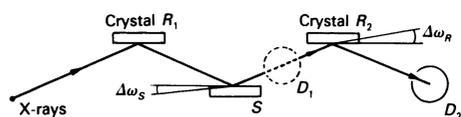


Fig. 5.3.3.11. Schematic representation of the triple-crystal spectrometer developed by Buschert (1965) (after Hart, 1981).

with an oscillating slit was proposed by Korytár (1984). This method permitted simultaneous recording of two rocking curves from two locations on a crystal. Precision of 3 parts in  $10^7$  was reported. The method has been applied for the measurement of growth striations in silicon.

The main disadvantage of double-crystal spectrometers, in their basic form (Fig. 5.3.3.8), is that they cannot be used for measurements on an absolute scale. Combination of the double-crystal arrangement with the system proposed by Bond (1960) makes it possible to recover the origin of the angular scale and thus such an absolute measurement, but the reported precision is rather moderate.

There are two other ways to overcome this difficulty in pseudo-non-dispersive methods: addition either of a third crystal (more accurately, a third reflection) (§5.3.3.7.2) or of a second source (a second beam) (§5.3.3.7.3). Such arrangements require additional detectors. Combinations of both techniques are also available (§5.3.3.7.4).

### 5.3.3.7.2. Triple-crystal spectrometers

Higher precision than that obtained with the double-crystal arrangements (§5.3.3.7.1) can be achieved by means of triple-crystal diffractometers. Arrangements specially designed for the determination of lattice-parameter changes are described by Buschert (1965) and Skupov & Uspeckaya (1975), and reviewed by Hart (1981).

The principle of the triple-axis spectrometer is shown in Fig. 5.3.3.11. The arrangement consists of one standard crystal  $S$ , ultimately replaced by the sample under investigation, and two reference crystals  $R_1$  and  $R_2$ . The principle of the measurement is as follows. First, the crystals  $S$ ,  $R_1$ , and  $R_2$  are set to their diffraction (peak) positions using two detectors  $D_1$  and  $D_2$ . Then the standard crystal  $S$  is replaced by the sample and the new peak position is found by means of  $D_1$  when the sample is turned from its original position to its reflecting position. The angle of rotation of the sample  $\Delta\omega_s$  depends on the lattice-parameter difference  $\Delta d$  between the sample and the standard. The relation is given by (Hart, 1981)

$$\Delta\omega_s = -\tan \theta \Delta d/d. \quad (5.3.3.40)$$

Next, the second reference crystal  $R_2$  is turned through the angle  $\Delta\omega_R$  to its diffracting position, the intensity being controlled with the second detector  $D_2$ . From the geometry of the arrangement,

$$\Delta\omega_R = 2\Delta\omega_s. \quad (5.3.3.41)$$

Because the origin of the  $\omega_s$  scale is lost during the crystal exchange, this second angle of rotation ( $\Delta\omega_R$ ) is used to determine  $\Delta d$  rather than the first one ( $\Delta\omega_s$ ), by using (5.3.3.41) and (5.3.3.40).

The diffraction profiles observed in the second detector, described by Hart (1981),

$$h(\theta)_R = \int_{-\infty}^{\infty} R^2(\theta') R(\theta' - \theta) d\theta', \quad (5.3.3.42)$$

are not symmetric but can be as narrow as  $0.1$ – $1''$ , so that a precision of 2 parts in  $10^8$  is possible.

The main experimental problem here is to adjust the tilts of the crystals. The errors resulting both from the crystal tilts and from the vertical divergence were discussed by Skupov & Uspeckaya (1975).

Triple-crystal spectrometers are often applied as lattice-spacing comparators, when very small changes of lattice parameters ( $10^{-8} \leq |\Delta d|/d \leq 10^{-6}$ ) are to be detected, in