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ATOM LOCATION BY ELECTRON CHANNELING ANALYSIS

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For many years the orientation dependence of the characteristic x-ray emission close to a Bragg reflection has been regarded as a hindrance to accurate microanalysis, and a random incident beam direction has always been recommended for accurate composition analysis. However, this orientation dependence can be put to use to extract information on the lattice location of foreign atoms within the crystalline matrix. Close to a Bragg reflection a standing wave pattern is set up by the electron wavefront, which results in channeling of the electron current along or between the Bragg reflecting planes.[1] When a standard "two-beam" condition is set up with the incident beam just outside the Bragg reflecting planes, the electron current is channeled predominantly between these planes. This results in good electron transmission for imaging purposes, and a low yield of characteristic x-ray emission. Conversely, when the electron beam is incident just inside the Bragg reflecting condition, the electron current is channeled along the planes which gives a high yield of x-rays. This effect can be used as the basis for atom location studies, by comparing the variations seen in the x-ray yield from the matrix and impurity atoms, when the beam is tilted between these two conditions.

The first studies of this nature were referred to as "ALCHEMI" Atom Location by Channeling Enhanced Microanalysis.[2-4] They were performed on minerals in which a projection could be found to reveal a layer structure of the type ABAB, where the B planes consisted of only light atoms, and the possible sites for the impurity elements were contained in either the A or the B planes. The fractions of impurities in the two possible crystal sites could be quantitatively determined

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by a ratio technique which avoided detailed dynamical theory calculations of the precise electron intensity profiles achieved in particular experimental conditions. However, the analysis will break down if the impurity is not contained within the A or B planes, and many materials do not have a projection with a suitable layer structure. Here a generalization of the technique is described which is applicable to any crystal structure including monatomic crystals, and can quantitatively determine substitutional fractions of impurities.

The technique was referred to as electron channeling analysis, by analogy with the closely related and widely used bulk technique of ion channeling analysis,[5] and was developed for lattice location studies of dopants in semiconductors at high spatial resolution.[6] Only two spectra are required for each channeling analysis, one in each of the channeling conditions described above. If the matrix and dopant x-ray yields vary identically between the two orientations then the dopant necessarily lies within the reflecting matrix planes. If the dopant x-ray yield does not vary the dopant atoms are randomly located with respect to the matrix planes. Examples of the electron channeling analysis of these two situations are shown in Fig. 1a and 1b, respectively. The exact matrix yield variation depends on the exact orientations chosen, the sample thickness, and the beam convergence, and are slightly different in Fig. 1a and b. However, the ratio technique again avoids the need for calculations of the electron intensity profiles.

For highest accuracy of electron channeling analysis the dopant should be uniformly distributed through the sample thickness, since the standing wave pattern slowly decreases in amplitude and changes in form as it propagates through an increasing thickness of crystal. These samples were prepared by implanting (100)Si specimens with $^{121}Sb^{+}$ ions at different energies and doses

chosen so as to produce an approximately uniform dopant concentration of 1.6 at. % in the top 100 nm of the samples. After solid-phase-epitaxial (SPE) regrowth in a furnace at 550°C for 30 min. a supersaturated solid solution is formed free of extended defects with the dopant trapped in substitutional sites.[7] The Sb concentration exceeds the retrograde maximum solid solubility by approximately 20 times. A bulk ion channeling analysis of this material confirmed an Sb profile with uniform concentration and showed that greater than 99% of the Sb was in substitutional sites. This material is ideally suited for an electron channeling study and gave the results shown in Fig. 1a.

Simply by heating this alloy to 1000°C for 30 minutes the dopant in excess of the solubility limit was precipitated. The precipitates were coherent with the {111} planes but in a random orientation with respect to the {220} channeling planes,[8] and the spectra shown in Fig. 1b were obtained. It should be possible to determine the substitutional fraction F_S of the dopant in the region analyzed directly from the two spectra obtained in the two channeling orientations, by defining

$$F_S = \frac{\Delta X_{Sb}-1}{\Delta X_{Si}-1} \qquad (1)$$

where ΔX is the ratio of the x-ray yields. Experimentally however, it was found that the Sb variation systematically exceeded the Si variation, giving F_S values greater than unity. This is due to the different spatial localization of the Sb and Si inner shell excitations. A fast electron may excite the shell from a considerable distance away, referred to as the impact parameter b. An average impact paramter b_{RMS} for x-ray generation is obtained by integrating over all scattering angles, weighted by the inelastic cross-section,[9] to give

$$b^{RMS} = \frac{\hbar v}{\Delta E}\left[\ln\left(\frac{4E}{\Delta E}\right)\right]^{-1/2} \qquad (2)$$

where E is the incident beam energy; and ΔE is the inner shell binding energy. For 100 keV electrons, we find $b_{Sb}^{RMS} = 0.0120$ nm $> b_{Si}^{RMS} = 0.0249$ nm. While both are small compared to the {220} interplanar spacing of d = 0.192 nm, so that both x-ray intensities show good channeling effects, the greater localization of the Sb excitation leads to a yield variation slightly greater than for Si. To take account of this differing localization of impurity and matrix excitations, we define

$$F_s = \frac{1}{C}\frac{(\Delta X_{Sb}-1)}{(\Delta X_{Si}-1)} \qquad (3)$$

where C is a delocalization correction factor.

The experimental results from the alloy in Fig. 1a determined that C = 1.10 ± 0.04 for {220} planar channeling analysis of Sb in Si.[6] Delocalization effects will be more apparent with lower energy excitations, for example, boron will be mostly delocalized, but with higher energy excitations, such as for As or Bi dopants in Ge, probably no correction factor would be necessary. Lower energy excitations of neighboring elements, such as for P in Si should also need no correction since they will be delocalized to similar extents. The effect of delocalization is less pronounced for larger interplanar spacings, possibly why no effects were noticed in the ALCHEMI studies of minerals.[2-4]

The effects of non-uniform dopant profiles have been investigated using Si(100) implanted with $^{121}Sb^{+}$ at a single energy. The modulations of the standing wave intensity profile gradually dminish as the beam propogates through an increasing thickness of sample. If the dopant is concentrated near the

electron entrance surface of the sample, it will show a larger yield variation, even after correcting for delocalization effects, than the matrix, whereas if the dopant is concentrated near the electron exit surface of the sample, it will show a reduced yield variation. For samples 100 nm thick the errors introduced were found to be less than 10%.[10]

The process of precipitation of the Sb has also been studied by a combination of electron channeling analysis and TEM. The fraction of Sb in precipitate form was measured from the size distribution observed in the TEM image, and compared to the nonsubstitutional fraction of dopant determined from the same region by electron channeling. Results are shown in Fig. 2 from the sample of Fig. 1a subjected to a sequential anneal between 680°C and 950°C to precipitate out increasing amounts of dopant. At the end of the sequence, where the precipitates are randomly oriented, as in Fig. 1b, the two measurements agree closely. However, in the early stages of precipitation, there appears to be over twice as much nonsubstitutional dopant than can be accounted for in precipitates. TEM images taken under dynamical diffraction conditions show matrix strains around these precipitates. If they were coherent with the silicon lattice, but with their planes in an interstitial location between the Si planes, then the Sb in the precipitates, rather than showing no x-ray yield variation, would show a reverse channeling effect to the Si. The total Sb yield variation would be reduced by twice as much as for randomly located Sb, as is seen experimentally. If the coherent precipitates were aligned with the Si planes, the Sb in them would appear substitutional, and the points in Fig. 2 would lie on the other side of the diagonal line. By combining electron channeling and TEM, information can be deduced concerning the interface between the matrix and precipitates. It should be possible to study other interfaces by such techniques.

All electron channeling studies to date have used a planar channeling geometry. Recently the use of an axial channeling geometry has shown a greatly enhanced channeling effect. The beam is tilted from the exact zone axis to just outside the major reflecting planes comprising the zone axis, and the electron wavefront propogates in columns, either along the strings of atoms or between them, producing the enhanced channeling effect. In addition, the delocalization correction factors are reduced. The yield variations for axial electron channeling are roughly the product of the yield variations for the low-order planes contained in the zone axis. The increased yield variation is a great advantage since the error in the channeling analysis depends on the error of the difference between the two spectra. Axial channeling will allow shorter analysis times, and the analysis of smaller quantitites of dopants, either lower concentrations or smaller sample areas. Atom location analysis at high spatial resolution around precipitates, grain boundaries, or dislocations will be possible.

REFERENCES

1. P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley and M. J. Whelan, Electron Microscopy of Thin Crystals, Butterworth, London (1965).
2. J. C. H. Spence and J. Tafto, p. 523 in Scanning Electron Microscopy/1982/II, SEM Inc. AMF O'Hare, Ill. (1982).
3. J. Tafto and J. C. H. Spence, Science 218, 49 (1982).
4. J. C. H. Spence and J. Tafto, J. Microscopy 130, 147 (1983).
5. B. R. Appleton p. 97 in Defects in Semiconductors, ed. by J. Narayan and T. Y. Tan, Elsevier, New York (1981).
6. S. J. Pennycook, J. Narayan, and O. W. Holland, Appl. Phys. Lett. 44, 547 (1984).
7. J. Narayan, O. W. Holland, and B. R. Appleton, J. Vac. Sci. Technol. B1, 871 (1983).
8. S. J. Pennycook, J. Narayan, and O. W. Holland, J. Appl. Phys. 54, 6875 (1983).
9. S. J. Pennycook, Contemp. Phys. 23, 371 (1982).
10. S. J. Pennycook, J. Narayan, and O. W. Holland, in Electron Microscopy of Materials, Vol. 31 of the Materials Research Society, ed. by W. Krakow, Elsevier, New York (1984, in press).

FIGURE CAPTIONS

Fig. 1. X-ray spectra from electron channeling analysis of Si-Sb alloys 99% and 5% substitutional. Insert shows schematically beam tilt conditions showing incident and diffracted beams with respect to Kikuchi lines.

Fig. 2. Open circles show results of sequential anneal referred to in text. Solid symbols are results of single anneals analyzed by electron channeling (circles) and bulk ion channeling (triangles) showing good agreement.[10]

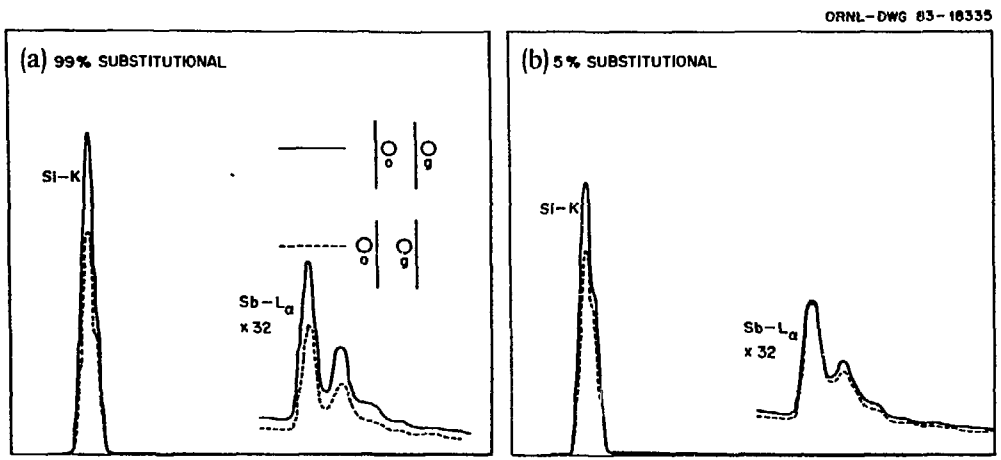
ORNL-DWG 83-16335
(a) 99% SUBSTITUTIONAL
Si-K
Sb-Lα
x 32
(b) 5% SUBSTITUTIONAL
Si-K
Sb-Lα
x 32

Fig. 1

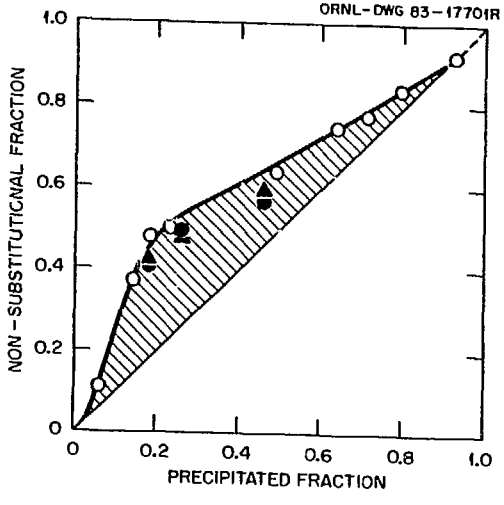
ORNL-DWG 83-17701R
NON-SUBSTITUTIONAL FRACTION
PRECIPITATED FRACTION
0
0.2
0.4
0.6
0.8
1.0

Fig. 2