

# Spatially resolved measurement of substitutional dopant concentrations in semiconductors

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It is shown that a simple ratio technique based on the electron channeling phenomenon can be used to measure substitutional fractions of dopants in submicron-sized regions of semiconductors. Samples were made from  $^{121}\text{Sb}^+$  implanted Si, solid-phase-epitaxially regrown, and analyzed by ion channeling. One sample was sequentially annealed so as to precipitate out various fractions of the dopant in excess of the solubility limit. In the fully annealed sample electron channeling measurements could quantitatively determine the fraction of Sb in precipitate form since it was randomly located with respect to the matrix. In the partially annealed sample electron channeling indicated a larger nonsubstitutional fraction than could be accounted for by observed precipitates.

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The electrical activation of dopants in semiconductors is determined by their incorporation into substitutional lattice sites. Ion channeling techniques lend themselves to accurate determination of lattice location and concentration of dopants in semiconductors.<sup>1</sup> However, the area of the samples from which meaningful information can be attributed is of the order of millimeters. In advanced integrated circuit devices where active areas are smaller than a micron, we need a technique with spatial resolution in the submicron range.

In this letter, we discuss the use of electron channeling for the determination of lattice location of dopants in semiconductors, where the size of the analysis area can be as small as the electron probe forming capability of the electron microscope allows, possibly of nanometer dimensions. These electron channeling effects are similar to x-ray channeling effects which have been used for lattice location studies,<sup>2,3</sup> except for the increased spatial resolution which is obtained by the fine probe forming capabilities of an advanced electron microscope. Electron channeling effects have long been regarded as a hindrance to accurate microanalysis, but recently, the effect has been exploited for the site location of trace elements in minerals.<sup>4,5</sup> Minerals were chosen having two different types of matrix atoms distributed between two different parallel planes. In the case of silicon, there is a single matrix-atom type lying on a single set of planes, and it has been suggested that a quantitative determination of site occupancy requires an absolute measurement of x-ray yield.<sup>6</sup> Here we show that a ratio method can be used as a test of substitutionality, and further, that if some of the dopant is nonsubstitutional, but known to be randomly arranged with respect to the matrix planes, then the substitutional fraction of dopant can be determined quantitatively by the ratio technique.

The electron channeling effect occurs when a parallel beam of electrons is incident on a crystal close to a Bragg reflecting orientation. As the electron beam propagates through the crystal, it sets up a standing wave intensity profile normal to the Bragg planes with the same periodicity as the planes. By small deviations of the incident beam direction either inside or outside the exact Bragg orientation, the

maxima in the standing wave pattern can be made to lie either on the crystal planes or between them, respectively.<sup>7</sup> The variation of the matrix x-ray yield between the two channeling orientations depends sensitively on the crystal thickness and the exact two orientations chosen. But, if the dopant is uniformly distributed through the crystal thickness, and the dopant and matrix x-ray yields vary identically between the two channeling orientations, then the dopant necessarily lies within the matrix channeling planes. Successive measurements along two or more planes (triangulation) can be used to determine if the dopant is substitutional. The ratio technique should work well for trace elements even in a monatomic matrix as a test of substitutionality and avoids the need for detailed dynamical theory calculations of the electron intensity profile. The logic of the arguments is essentially that employed for ion scattering studies. Ion and electron channeling experiments are complementary; ion channeling experiments have good depth resolution, but their lateral resolution is of the order of millimeters, whereas electron channeling measurements are integrated over depth, but have lateral resolution potentially on a nanometer scale.

We have studied (100) Si specimens implanted with  $^{121}\text{Sb}^+$  ions at different energies and doses chosen so as to produce an approximately uniform dopant concentration of 1.6 at.% down to 100 nm. 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.<sup>8,9</sup> An ion channeling analysis of this material is provided in Fig. 1, which shows a Sb profile with uniform concentration and with greater than 99% of the Sb in substitutional sites. This material is ideally suited for an electron channeling study. Thin samples were prepared by a chemical thinning procedure and studied in a Philips EM 400 electron microscope equipped with an ORTEC EEDS II energy dispersive x-ray analysis system. Electron channeling analysis was performed using a 220 planar channeling orientation on areas typically 300 nm in diameter and less than 100 nm in thickness. The thickness was measured from thickness fringes<sup>7</sup> and by convergent beam electron diffraction<sup>10</sup> at the exact Bragg condition. The micro-

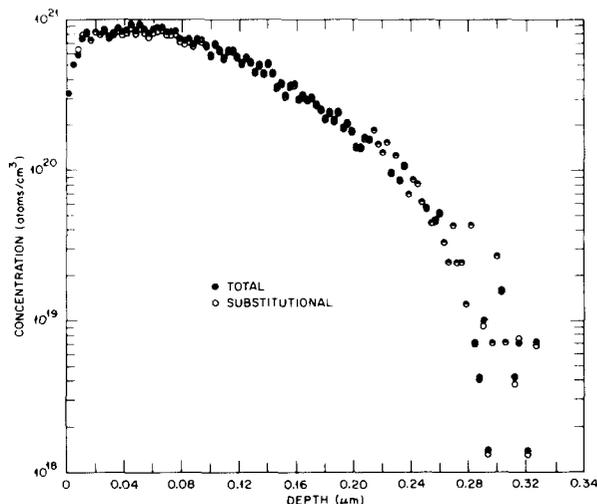


FIG. 1. Ion channeling analysis showing total and substitutional concentrations of Sb in Si as a function of depth.

scope was switched between three beam tilt conditions: first at the exact Bragg condition, required for thickness measurement, second inside, and third outside the Bragg reflecting conditions. The last two are required for a single channeling analysis as shown in Fig. 2(a). Spectra were collected for 500 s, changing between the two channeling orientations each 100 s, so as to minimize possible errors due to specimen or microscope drift, and analyzed by subtracting a fitted background spectrum and integrating the counts in the characteristic Si-K and Sb- $L_{\alpha}$  peaks over a 140- and 160-eV energy window, respectively.<sup>11</sup> Typically between 2000 and 3000 counts were counted in the Sb energy window. The total spectrum count rate was kept below 2000 counts per second to avoid Si-K pulse pile-up from contributing to the Sb peak. Absorption of x rays was negligible in the thickness used (approximately 100 nm), as was the effect of the few counts obtained when the beam was passed through the hole in the sample.

The results of {220} and {400} planar channeling are shown from 10 areas in Table I. The ratios of the Si and Sb x-ray peaks,  $\Delta X_{Si}$  and  $\Delta X_{Sb}$ , collected in the two channeling orientations, are shown together with the ratio of the channeling effects given by  $(\Delta X_{Sb} - 1)/(\Delta X_{Si} - 1)$ . The yield variations are smaller for {400} channeling, so that the  $\Delta X$  values are closer to unity. The {111} channeling gave even smaller x-ray yield variations, probably due to the double structure of these planes, and since the error in the channel-

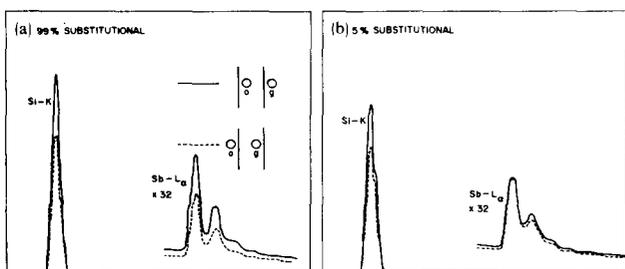


FIG. 2. X-ray spectra from electron channeling analysis of Si-Sb alloys 99% and 5% substitutional. Insert shows schematically the beam tilt conditions showing incident and diffracted beams with respect to the Kikuchi lines (traces of the matrix planes).

TABLE I.

Plane	$\Delta X_{Si}$	$\Delta X_{Sb}$	$\Delta X_{Sb} - 1/\Delta X_{Si} - 1$
(220)	1.4975	1.5294	1.06
(220)	1.5270	1.6040	1.15
(220)	1.6254	1.7061	1.13
(220)	1.4387	1.4593	1.05
(220)	1.4202	1.4575	1.09
			Average 1.10 $\pm$ 0.04
(400)	1.2479	1.2802	1.13
(400)	1.2385	1.2797	1.17
(400)	1.2270	1.2908	1.28
(400)	1.2105	1.2417	1.15
(400)	1.2084	1.2316	1.11
			Average 1.17 $\pm$ 0.07

ing measurement is dominated by the error in the *difference* between the two Sb peaks, {111} channeling was not used for site location. It is quite clear from Table I that the Sb variation systematically exceeds the Si variation. This is expected, due to the different spatial localization of the Si and Sb excitations. An electron of velocity  $v$  can excite an atomic shell of binding energy  $E$  if it passes closer to the shell than a distance normally referred to as the impact parameter  $b = \hbar v/E$ , where  $\hbar$  is Planck's constant.<sup>12</sup> So although the inner atomic levels are themselves highly localized, the excitations are delocalized over this distance. With increasing delocalization of the excitation, smaller variations in the x-ray yield are observed, until when  $b$  exceeds half the interplanar spacing, no variation in yield is observed. For Si-K,  $E = 1839$  eV while for Sb- $L_{\alpha}$ ,  $E = 4132$  eV so that the Si-K excitation is less localized than the Sb- $L_{\alpha}$ , giving rise to the smaller x-ray yield variation observed between the two channeling conditions. A theoretical prediction of  $(\Delta X_{Sb} - 1)/(\Delta X_{Si} - 1)$  for 100 keV electrons (to be reported elsewhere), assuming the Sb to be 100% substitutional, gives 1.10 for {220} channeling and 1.21 for {400} channeling, in good agreement with experimental values. The effect of delocalization is less pronounced for larger interplanar spacings, possibly why no effects were noticed in the channeling studies of minerals.<sup>4,5</sup>

Since the ion channeling results show the Sb to be greater than 99% substitutional, these experimental results may be taken as representing the correction factors required for the effects of delocalization. These effects will be more apparent with lower energy excitations, for example, boron will be mostly delocalized. Channeling measurements using higher energy excitations, such as for As or Bi dopants in Ge, will probably need no correction factor. 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.

If a fraction of the dopant is nonsubstitutional a problem may arise. For example, if 10% of the dopant was randomly arranged, its x-ray yield variation would be only 90% of the matrix x-ray yield variation. However, if 10% of the dopant was interstitial then this fraction would show a reversed channeling contrast, so that the overall dopant x-ray yield would vary by only about 80% of the matrix yield variation. This is similar to flux peaking effects in ion channel-

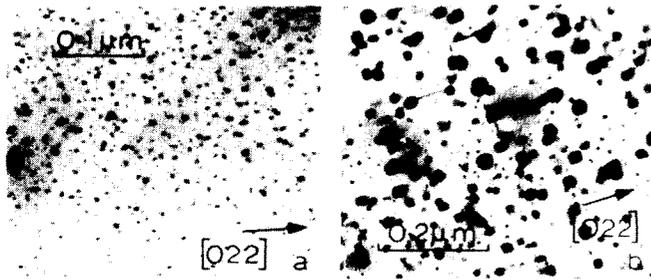


FIG. 3. Transmission electron micrographs of Si-Sb alloys showing formation and growth of precipitates during an annealing sequence (see text for details); (a) after 680 °C/20 min anneal, (b) after 950 °C/20 min anneal.

ing.<sup>13</sup> To determine the substitutional fraction we need one or other situation to prevail, and to know which. A nonsubstitutional fraction was induced by heating the supersaturated Si-Sb alloy for 20 min at 680, 700, 720, 750, 800, 850, 900, and 950 °C, to precipitate out increasing amounts of dopant. Electron channeling analysis was carried out after each anneal. Figure 2(b) shows the x-ray spectra obtained after the final anneal, when the Sb x-ray yield variation was very small. Fully precipitated samples have been studied previously, and it was shown that the largest precipitates were partially coherent with Si{111} planes, but not coherent with Si{220} planes.<sup>14</sup> In this case, the precipitated Sb has a random location with respect to the {220} planes, and the substitutional fraction of Sb is given by

$$F_s = \frac{1 \Delta X_{Sb} - 1}{C \Delta X_{Si} - 1},$$

where  $C = 1.1$  is the delocalization correction factor determined previously. The fraction of Sb in precipitates was separately determined from micrographs of the channeled areas, examples are shown in Fig. 3. Using the precipitate size distribution and local sample thickness, the amount of Sb precipitated per unit volume was measured. The total Sb concentration in the region was also measured, using the x-ray spectrum taken with the crystal tilted slightly to a non-diffracting orientation, and was found to vary by about  $\pm 10\%$  from the mean implanted concentration. The results are shown in Fig. 4, where the nonsubstitutional fraction, measured by electron channeling, is plotted against the fraction of Sb in precipitate form, measured from the micrographs. After the highest temperature anneals, the two estimates agree closely, and the remaining substitutional dopant is consistent with the solubility limit of Sb in silicon. In the early stages of precipitation there appears to be over twice as much nonsubstitutional dopant than can be accounted for in the observed precipitates. There are several possible explanations for this. First, during this period the Sb is diffusing rapidly by an interstitialcy mechanism, caused by the diffusion of a high concentration of the interstitials which had been trapped during SPE growth.<sup>15</sup> Some of the Sb in solution may, therefore, be lying out of a regular lattice position. Alternatively, small dopant complexes may be formed in which, again, the Sb is pulled off its substitutional lattice sites. Such complexes would be too small to be observed in the electron microscope. A third possibility is that the smallest precipitates are coherent with the Si channeling planes, with the precipitate planes located interstitially between the

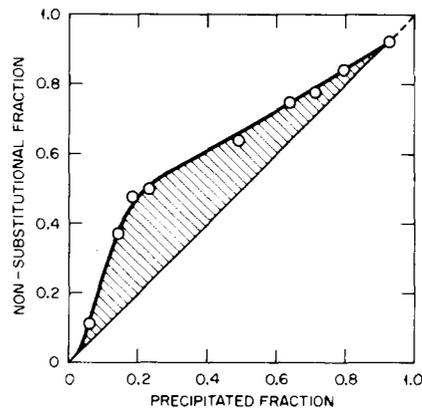


FIG. 4. Nonsubstitutional fraction of Sb determined by electron channeling plotted against fraction of Sb in precipitate form. See text for discussion of the shaded area.

Si planes. The Sb channeling yield variation would be reduced by about twice as much as for randomly located precipitates, giving the false impression of a larger nonsubstitutional concentration. Coherency strains around very small precipitates are not visible in transmission electron micrographs.

In conclusion, we have shown how electron channeling, using a simple ratio technique, can be used to determine the substitutional fraction of dopants in semiconductors, provided the effects of different localization of the matrix and dopant excitations are considered. Furthermore, in samples where it is known that the nonsubstitutional dopant is randomly located with respect to the channeling planes, then the ratio technique gives a quantitative measure of the substitutional fraction of dopant. In the partially precipitated Sb-Si alloy samples, the channeling results indicated either the formation of coherent precipitates with their planes located interstitially with respect to the Si{220} planes, or that some of the Sb left in solution was not lying in substitutional sites.

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