Site-Selective Doping of Compound Semiconductors by Ion Implantation of Radioactive Nuclei

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Sn impurity atoms have been selectively inserted on the two different substitutional lattice sites in the III-V semiconductors GaP, GaAs, GaSb, InP, InAs, and InSb. Radioactive $^{115}$In$^+$ and $^{115}$Sb$^+$ ions which decay to the Mössbauer state of $^{115}$Sn have been implanted. From the isomer shifts determined in Mössbauer-emission experiments it is concluded that the implanted In and Sb ions selectively populate III and V sites, respectively.

Doping of semiconductors by ion-implantation techniques is widely utilized for technological as well as for research applications. Mainly ions of the desired dopant elements have been implanted. Here we report on a new method, particularly attractive for doping of compound semiconductors. The radioactive ions that are implanted decay to the desired dopant element. As shown in the present investigation, this method enables a selection of the lattice site for, e.g., amphoteric dopants like Sn in III-V semiconductors. Although technological applications might be hampered by the relatively large amounts of radioactive needed, the method has promising aspects for microscopic investigations of dopant properties.

Radioactive $^{115}$Sb$^+$ ions were implanted at room temperature at an energy of 80 keV to a dose of $\sim 10^{13}$ atoms/cm$^2$ with an isotope separator. The $^{115}$Sb activity was obtained from a bombardment of natural tin with 20-MeV $\alpha$ particles by a procedure described previously. The radioactive $^{115}$In$^+$ ions were obtained as proton induced fission products in a uranium carbide target irradiated by 600-MeV protons from the CERN synchrocyclotron. Following on-line mass separation in
the ISOLDE mass separator, the 60-keV ions were implanted at a rate of \( \sim 5 \times 10^9 \) ions/s for \( \sim 4 \) min. All implanted semiconductor single crystals were n-type material.

The experimental problems of measuring Mössbauer emission spectra for the weak \(^{119}\text{Sb}\) sources (\( T_{1/2} = 38 \) h, source strength \( \sim 1 \mu\text{Ci} \)) and the strong \(^{119}\text{In}\) sources (\( T_{1/2} = 2.1 \) min, source strength \( \sim 10 \text{ mCi} \)) were solved by the application of fast resonance detectors. Extreme source strength was essential for the \(^{119}\text{In}\) experiments since spectra had to be measured within a few minutes. Details of the experimental procedures will be published elsewhere.

Two Mössbauer spectra measured at \( \sim 77 \) K from implantations of \(^{119}\text{In}\) into InP at room temperature are shown in Fig. 1. Spectrum a was measured within 4 min after the implantation, spectrum b within 4 min after an annealing of the sample for 1 min at \( 270 \) °C subsequent to the implantation. The spectra have been analyzed in terms of two independent emission lines as indicated in the figure. The broadened line at \( \delta = 2.8 \) mm/s is seen to decrease after the annealing of the sample. This is attributed to the annealing of a parent \(^{119}\text{In}\)-vacancy complex, from which this line originated. Similar impurity defects have been found in most room-temperature implanted compound semiconductors. Their Mössbauer parameters and annealing properties will be reported elsewhere. Since the complex defects annealed between 200 and \( 400 \) °C for all implanted semiconductors, predominantly single lines were left over in all spectra after an appropriate annealing. Such a spectrum for an Sb implantation in InP is shown in Fig. 2. The single emission lines were in all cases nearly unbroadened (\( \sim 10\% \)) indicating that the implanted atoms are in locally undisturbed cubic surroundings.

Figure 3 displays the isomer shifts of the single lines from annealed samples versus the lattice constants of the host materials together with the values for substitutional Sn in group-IV elements. While the isomer shifts from the Sb implantation in the III-V compounds fall on the line for group-IV elements, the values from the In implantations are systematically lower. Substitutional Sn in group-IV elements is known to have electronic structures similar to those of the host materials due to a redistribution of the Sn valence electrons according to the bond character of the hosts. If an analogous redistribution is assumed for the Sn impurities in III-V hosts, the difference in isomer shifts for In and Sb implantations, respectively, can be attributed to the population of the two different substitutional lattice sites in these compounds. As a consequence of the ionicity of the compound bonds in comparison to the covalent bonds of the elemental semiconductors, the electron density at the nucleus is unequal for these two sites. From chemical considerations, it may be expected that the electron density and hence the isomer shift is lower for the III than for the V site. Therefore, from the experimental re-
It is interesting to note that the above assignments are in accordance with those from Mössbauer experiments on implanted $^{119m}$Sn in GaAs, where it was concluded that Sn occupies the Ga site for annealed samples, in perfect agreement with electrical measurements. Obviously, for a detailed understanding of the Mössbauer parameters, quantitative model calculations are required. Nevertheless, qualitatively the basic features seem to be explained by the above considerations.

The method of site-selective doping is expected to be applicable also for other dopants in III-V or II-VI compound semiconductors.

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