Formation of In-As Complexes in Silicon Observed by the Perturbed–Angular-Correlation Technique

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The formation of In-As pairs and clustering of As atoms in Si was studied via their electric field gradients by use of the perturbed–angular-correlation technique and ^{111}In as probe atoms. Clustering of As atoms strongly depends on As concentration and temperature treatment. The observed pairing between In and As atoms seems to be typical for the interaction between acceptor and donor atoms in Si and it explains the earlier observation that the presence of donor atoms influences the lattice site of acceptor atoms.

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In semiconductors like Si, the electronic properties are determined to a large extent by the clustering and lattice site of dopant atoms and by the method of sample annealing in case of ion implantation. Up to now, the information delivered by microscopic techniques has been limited.[1] In Si the formation of Co dimers was observed by Mössbauer spectroscopy[2] and the configuration of As pairs was reported by extended x-ray–absorption fine structure experiments.[3] The paramount data on lattice-site determinations came from the ion channeling technique, which revealed a significantly larger tendency of group-V than of group-III dopants for substitutional-site occupancy after implantation in Si.[4,5] If both types of dopants were present, however, for the group-III dopants an increase of the substitutional at the expense of the interstitial fraction was observed.[4] The existing lattice-site information supplied by channeling can be considerably augmented by perturbed $\gamma\gamma$ angular correlation (PAC) measurements, because this method uses the site-specific electric field gradient (efg) to distinguish among impurity sites differing by their lattice-site location and/or local electronic environment. In metals, PAC measurements have provided a powerful method of identifying and labeling defect–solute-atom complexes and small solute-atom clusters[6]; but, up to the present time, no unique identification of defects in semiconductors has been achieved.[7] In this Letter, by employing PAC we show that in Si the group-III element In is strongly attracted by the group-V element As; furthermore, small As clusters are directly identified and their formation probability is studied as a function of As concentration and temperature treatment of the sample. Such cluster formation has been postulated in order to explain the reduction in the electrical carrier concentration for high-dose As-implanted Si samples.[8]

Radioactive ^{111}In atoms with 40 keV energy at 293 K were implanted into Si single crystals to give a calculated peak concentration of about 2 ppm, based on the measured ^{111}In activity and the ion range straggling. During this doping procedure some ^{111}Cd atoms were also unavoidably coimplanted, the presence of which, however, played a role only in the case of the lowest As concentration. Beforehand, the Si samples were doped with As atoms either from the melt, resulting in concentrations of 0.015, 0.26, and 0.43 at.% As, or by implantation and subsequent annealing, leading to concentrations of 0.07 and 0.11 at.% As within the relevant surface region. All As concentrations were determined by the Rutherford backscattering technique. The ^{111}In-implanted samples were isochronally furnace annealed (600 s) in a vacuum of better than 5×10^{-6} Torr and then vacuum quenched by removal from the hot zone. The PAC spectra were measured at 293 K.

The site-specific efg is measured during the decay of the ^{111}In probe atom to ^{111}Cd, which successively emits two γ rays. By use of four γ detectors, PAC time spectra $R(t)=A(\theta)G_2(t)$ were obtained, as shown in Fig. 1 [the coefficient $A(\theta)$ was -0.118 for $\theta=180°$ and 90° and was -0.107 for $\theta=180°$ and 71°]. Provided that all In atoms experience the same efg, the time dependence is described by[6]

$$G_2(t)=S_0+\sum_{n=1}^{3}S_n\cos(\omega_n t). \quad (1)$$

The coefficients S_n depend on the orientations of both the efg and the γ detectors with respect to the Si lattice. In the case of axial symmetry of the efg tensor about its largest component V_{zz} we get $\omega_n=n(3\pi/10)eQV_{zz}/h$, where Q is the electric quadrupole moment of the excited ^{111}Cd nucleus. In general, the efg tensor is described by the quadrupole coupling constant $\nu_Q=eQV_{zz}/h$ and the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$. If the In atoms occupy different sites with fractions f_i, $G_2(t)$ in Eq. (1) is split into

$$G_2(t)=\textstyle\sum_i f_i G_2^i(t), \quad (2)$$

where each site is characterized by ν_{Qi} and η_i.

Directly after ^{111}In implantation, the PAC spectra of all Si samples show a wide distribution of unresolved

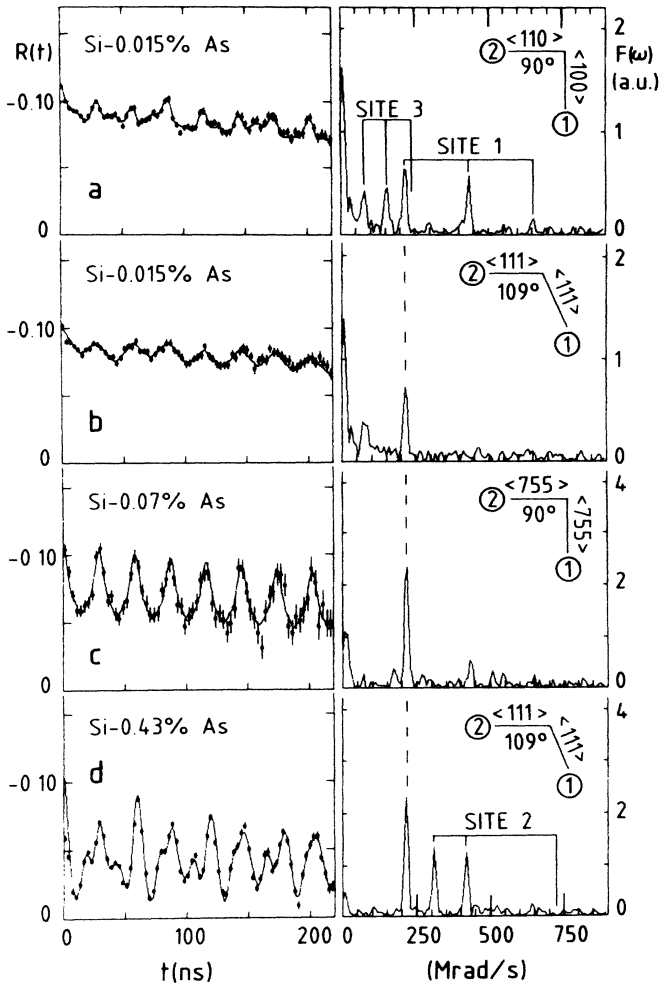

FIG. 1. Influence of the As concentration on the formation of three different In sites after annealing at (a)–(c) 1173 K, or (d) 900 K. Along with PAC spectra $R(t)$ their Fourier transforms $F(\omega)$ are shown. The arrangements of the four γ detectors are depicted by insets in the panels, for which detectors 3 and 4 are opposite to detectors 1 and 2. Note the change in the scaling of the ordinate for the lower two Fourier transforms.

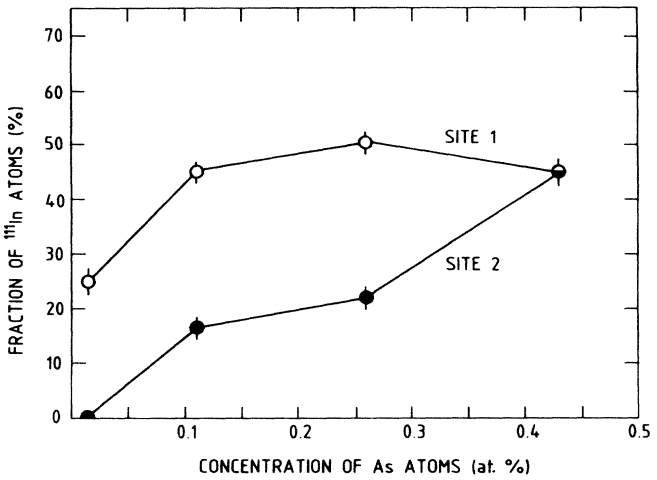

FIG. 2. The fractions of ^{111}In atoms located in sites 1 and 2, as functions of the As concentration in Si samples which were implanted with ^{111}In, annealed for 600 s at 900 K, and then vacuum quenched.

efg's which is well known from earlier PAC studies[7] and delivers no detailed information. However, after annealing of the samples above 700 K unique efg's occur as can be seen in the PAC spectra and their Fourier transforms $F(\omega)$ in Fig. 1; here, the Si samples contain 0.015%, 0.07%, and 0.43% As. A least-squares fit according to Eqs. (1) and (2) shows that for lower As concentration [Figs. 1(a)–1(c)] In atoms mainly experience an efg which is characterized by $\nu_{Q1}=229(1)$ MHz and $\eta_1=0$ (site 1); for higher As concentration [Fig. 1(d)] a second efg arises which is described by $\nu_{Q2}=238(1)$ MHz and $\eta_2=0.65(1)$ (site 2). The small values of S_2 and S_3 for site 1 in $F(\omega)$ of Figs. 1(b)–1(d), where the γ detectors were positioned close to or along a $\langle 111\rangle$ lattice direction (see insets in Fig. 1), indicate that the axially symmetric efg tensor has its symmetry axis along a $\langle 111\rangle$ lattice direction.[9] A comparison of the influence of different detector orientations on the S_n values [Figs. 1(a) and 1(b)] confirms this assignment. We will briefly refer to site 3, which is characterized by $\nu_{Q3}=83(1)$ MHz, $\eta_3=0$, with a $\langle 111\rangle$ symmetry axis, and was visible only for the lowest As concentration [Figs. 1(a) and 1(b)]. It might be caused by association of impurities other than As with In atoms since Rutherford backscattering measurements revealed that in the case of the 0.015%-As sample the concentration of coimplanted ^{113}In or ^{111}Cd atoms was comparable to the As concentration.

As a function of As concentration, Fig. 2 shows the fractions f_i of In atoms on either site 1 or site 2 after the samples were annealed at 900 K. By randomizing of the Si crystals the fractions of f_i were obtained from the fitted parameters $f_i S_n$. Obviously, the populations of both sites rise with increasing As concentration and the formation of site 2 involves more As atoms than that of site 1, as evidenced by the delayed increase of site 2. Neither site 1 nor site 2 was observed in previous PAC experiments where ^{111}In atoms were implanted in Si samples that did not contain As atoms.[7] These facts lead to an identification of both sites with In-As complexes, where site 2 contains *more* As atoms than site 1.

Regarding the formation of site 1 and site 2 the following conclusions can be drawn: At the highest As concentration, the fractions of the In atoms f_1 and f_2 occupying sites 1 and 2 both equal 45%. This behavior excludes a trapping of *mobile As atoms* by In atoms as the dominant reaction path for the formation of sites 1

and 2, since the formation of additional larger As clusters, caused by multiple trapping at the In atoms, would suppress such high site populations, especially the simultaneous population of two different cluster sizes with 45%. Therefore, one has to assume that the formation of both sites is mainly caused by *mobile In atoms;* this interpretation is supported by the diffusion coefficients for In and As in Si, yielding a 6 times higher mobility for In atoms at 900 K.[10] In the case of mobile In atoms, the formation of only one type of In-As complex (site 1) is expected as long as the As concentration is so low that As clusters are not present. Indeed, exclusively site 1 is observed for As concentrations of 0.015% and 0.07% As and therefore is identified with In-As pairs. Then, the occurrence of site 2 for higher As concentrations reflects the onset of As clustering leading probably first to As-As pairs; thus, site 2 should be identified with In-As_2 clusters. The fact that not always do all In atoms form As complexes can be explained by trapping of In atoms at other defects which produce an undetectably weak efg; at annealing temperatures around 900 K these sites account for almost all of the In atoms being not in site 1 or 2. However, with increasing As concentration these competitive traps obviously become less important and for the 0.43%-As sample 90% of all In atoms form complexes with As atoms.

The influence of annealing temperature T_A on the populations of site 1 and 2 is shown in Fig. 3 for the 0.43%-As sample. The temperature region below 900 K is dominated by the irreversible process of defect annealing, whereas in the region above 900 K the site

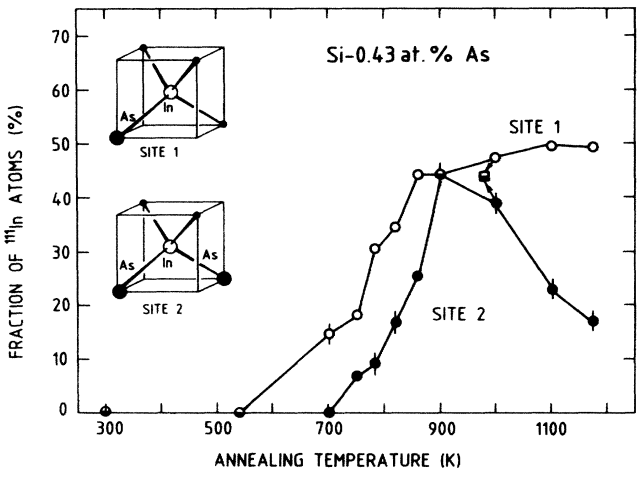

FIG. 3. Populations of site 1 (In-As atom pairs) and site 2 (In-As_2 complexes) observed during isochronal annealing (600 s) after ^{111}In implantation; the influence of a decreased cooling rate is demonstrated by the squared data points. For both sites, the insets show the microscopic structures that are in accordance with the symmetry of the measured efg tensors.

populations are reversible and depend on the particular annealing treatment. The In implantation at 295 K caused radiation damage and/or amorphization of the Si lattice. During annealing up to 900 K epitaxial recrystallization occurred and both types of In-As complexes were formed. Their formation at this temperature can be explained by radiation-enhanced mobility of both In and As atoms. Above 900 K the decrease of site 2 indicates that the In-As_2 clusters are less stable than the In-As pairs. The population of site 2 can be again increased by suitable heat treatment; for example, after annealing at 1000 K and a subsequent PAC measurement at 293 K the sample was annealed at 980 K and *slowly* cooled instead of vacuum quenched, which resulted in a restoration of the higher site population observed at 900 K (squared data points). This reversibility in the population of site 2 is observable for temperatures up to 1170 K, where the population had gone below 20%. That means that above 900 K the cooling rate determines the actual population of site 2, i.e., the clustering of As atoms: A high (low) cooling rate reduces (increases) the formation of As clusters. For a long time electrical resistivity data for As-doped Si have been known, which showed that either a too high As concentration (above 0.1% As) or a low cooling rate after thermal annealing reduces the fraction of electrically active As atoms.[8] This reduction in the electrical carrier concentration is precisely paralleled by a high site-2 population in the PAC experiments; therefore the reduction of electrically active As atoms finds its explanation in the formation of As clusters. Formation of these clusters was already postulated in earlier publications, but their direct detection was still missing.[8]

A formation of acceptor-donor pairs, like In-As, is predicted on the basis of a local chemical bond between acceptor and donor atoms which leads to a covalent bond similar to that governing the III-V compounds.[11] Within such a model, In atoms in Si should form pairs also with the other group-V elements. Indeed, we have first experimental indications for the pairing of In atoms with the donor atoms P and Sb, which is characterized by $\nu_Q = 179(1)$ and 271(1) MHz, respectively.[12] Thus the pairing between acceptor and donor atoms in Si can be regarded as a general phenomenon, which especially has to be taken into account in case of mixed implants of both types of dopant atoms. The formation of In-As pairs can also explain the enhanced population of group-III elements (In) in substitutional sites under the influence of group-V elements (As) as observed by channeling[4]; through the formation of In-As pairs, the In atoms are pulled onto substitutional lattice sites.

It is known that a reliable, quantitative interpretation of the measured efg tensors characterizing both In-As complexes is presently not possible because of a

lack of an appropriate theoretical description of the electronic structure around the probe nucleus. However, on the basis of the measured symmetry of the efg tensors, which in many cases successfully could be interpreted in the framework of a simple point-charge model, we propose the atomic configurations shown as insets in Fig. 3. Although the efg is observed at the daughter atom ^{111}Cd it can be assumed that the symmetry of the efg is also characteristic for the lattice site of the parent atom ^{111}In in the respective In-As complex; this has been shown by Mössbauer experiments in III-V semiconductors in the case of the parents ^{119}In and ^{119}Sb, which both decay into the daughter ^{119}Sn.[13] The atomic configuration shown for the In-As pair exhibits axial symmetry about a ⟨111⟩ direction of the Si lattice, in agreement with the experimentally observed ⟨111⟩ symmetry of the efg tensor of site 1. On the basis of the ⟨110⟩ arrangement of As pairs observed by extended x-ray-absorption fine structure,[3] the atomic configuration shown for the In-As_2 complex is proposed, which produces a nonaxial efg tensor in accordance with the measured efg of site 2. Our simple model is not able to account for any lattice relaxation, but channeling results indicate that off-center positions are not occupied by the In or As atoms involved in the formation of site 1 or site 2.[4,5]

In conclusion, the presented PAC experiments supply microcsopic information on clustering of As atoms and a strong attraction between acceptor and donor atoms in Si. With the advent of more refined self-consistent calculations of the efg,[14] also a direct interpretation of the observed complexes via their efg would become possible. In any case, more investigations by PAC can be expected regarding point-defect–solute atom complexes, the diffusion of dopant atoms, and the formation of atomic-sized clusters of dopant atoms, including the influence of furnace, laser, or flash light annealing.

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