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Do palladium–dopant pairs exist in silicon?

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Abstract

The local structure and stability of an impurity complex of palladium in silicon has been studied on an atomic scale by perturbed angular correlation spectroscopy using the ^{100}Pd/Rh probe nuclei. Palladium exists as an acceptor Pd^- in n-type silicon and donor $Pd^{+/2+}$ in p-type silicon. Owing to the Coulomb attraction between oppositely charged impurities, the probability of pair formation between palladium and dopants (P, As, Sb and B) seems to be quite favourable. In contrast, the impurity complex of the form Pd_{Si}–V_{Si} has been identified in highly doped n-type silicon by its characteristic electric field gradient. The density function theory calculations of electric field gradient (EFG) for Pd_{Si}–V_{Si} defect complex were consistent with the experimentally observed EFG.

Keywords: Palladium; Silicon; Perturbed angular correlation

1. Introduction

The formation and identification of In/Cd–dopant pairs (P, As, Sb etc.) in silicon [1] using perturbed angular correlation (PAC) technique has prompted similar measurements with the fast diffuser palladium (Pd) in silicon. The current interest of Pd in silicon is also motivated by its fast diffusion that changes significantly with dopant concentration. Moreover, DLTS measurements revealed that Pd exhibits deep levels in the band gap of silicon and prefers the single acceptor state (Pd^-) in n-type and single/double donor states ($Pd^{+/2+}$) in p-type silicon [2]. Therefore, the formation of Pd–dopant pair seems to be quite likely. The strong affinity of Pd to form Pd–dopant pairs allows Pd segregation gettering in silicon to be employed for many technological purposes. The PAC technique is based upon hyperfine interaction of the nuclear electric quadrupole moment of the probe nuclei with the electric field gradient (EFG) of the host lattice, requires a radioisotope probe with concentration of about 1 ppm or even less. For the present measurements we have utilized ^{100}Pd which decays to ^{100}Rh and in practice, the PAC measurement takes place after the radioactive decay of the parent probe, ^{100}Pd, at $I = 2$ excited isomeric state of the daughter isotope ^{100}Rh. The PAC experiment yields the quadrupole interaction frequency ν_Q, related to the electric field gradient V_{zz} by $\nu_Q = |eQV_{zz}/h|$, and the asymmetry parameter η. The component V_{zz}, *the strongest component of EFG tensor*, is calculated from above equation using the known value of the quadrupole moment $Q = 0.151\,b$ for the isomeric state $I = 2$ of ^{100}Rh [3].

The measured EFG reflects the local electronic structure information which, in turn, depends upon the atomic environment around the probe nuclei. Since the EFG vanishes for cubic or tetrahedral point symmetry, probe atoms like Pd/Rh give no PAC signal on substitutional sites. The symmetry lowering induced by defects will give rise to an EFG in the crystal lattice. The EFG is not only sensitive to impurity atoms and native defects close to the probe atom, but also to the actual strength of the relaxation around the probe atom. The direction of the main axis of the EFG gives very clear information about the symmetry of the corresponding complexes formed. Therefore PAC measurements will yield particularly useful information about the interaction of Pd/Rh probe atoms

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with the dopants/defects. In order to achieve an unambiguous identification of the defects characterized by the EFG, ab initio calculations based upon density functional theory in the local density approximation have been performed.

2. Experimental details

The probe atoms $^{100}\mathrm{Pd} \rightarrow {}^{100}\mathrm{Rh}$ are produced with the 14UD heavy-ion accelerator facility at the ANU, via the nuclear reaction $^{92}\mathrm{Zr}(^{12}\mathrm{C}, 4n)^{100}\mathrm{Pd}$, using a ^{12}C ion beam with an energy of 70 MeV. The reaction subsequently recoil implants the Pd nuclei with an energy up to 8 MeV, up to 3 μm deep into the single crystals of silicon. For the present measurements we have used the following single crystals of (1 0 0) orientation: n-type ($6.7 \times 10^{14}\,\mathrm{P\,cm^{-3}}$) and p-type ($1.9 \times 10^{15}\,\mathrm{B\,cm^{-3}}$), p-type ($1.9 \times 10^{19}\,\mathrm{B\,cm^{-3}}$), n-type ($5.8 \times 10^{19}\,\mathrm{P\,cm^{-3}}$), n-type ($4.3 \times 10^{19}\,\mathrm{As\,cm^{-3}}$) and n-type ($0.7 \times 10^{19}\,\mathrm{Sb\,cm^{-3}}$). In order to remove the radiation damage caused by the implantation, the samples were annealed under nitrogen atmosphere for 30 min in the temperature range 100–600 °C. The coincident counts were recorded at room temperature by the conventional PAC setup utilizing the (84–75) keV γ–γ cascade of $^{100}\mathrm{Pd}/^{100}\mathrm{Rh}$ probe nucleus. PAC time spectra $R(t)$, generated from the background-subtracted coincidence counts were least squares fitted with a three-site model (a) the probe atoms corresponding to unperturbed lattice sites (b) the probe atoms belonging to damaged zones resulting in an exponential fast decay of amplitude, and (c) probe atoms with well-defined unique interaction parameters having various distant defects in the first coordination shells.

3. Results and discussion

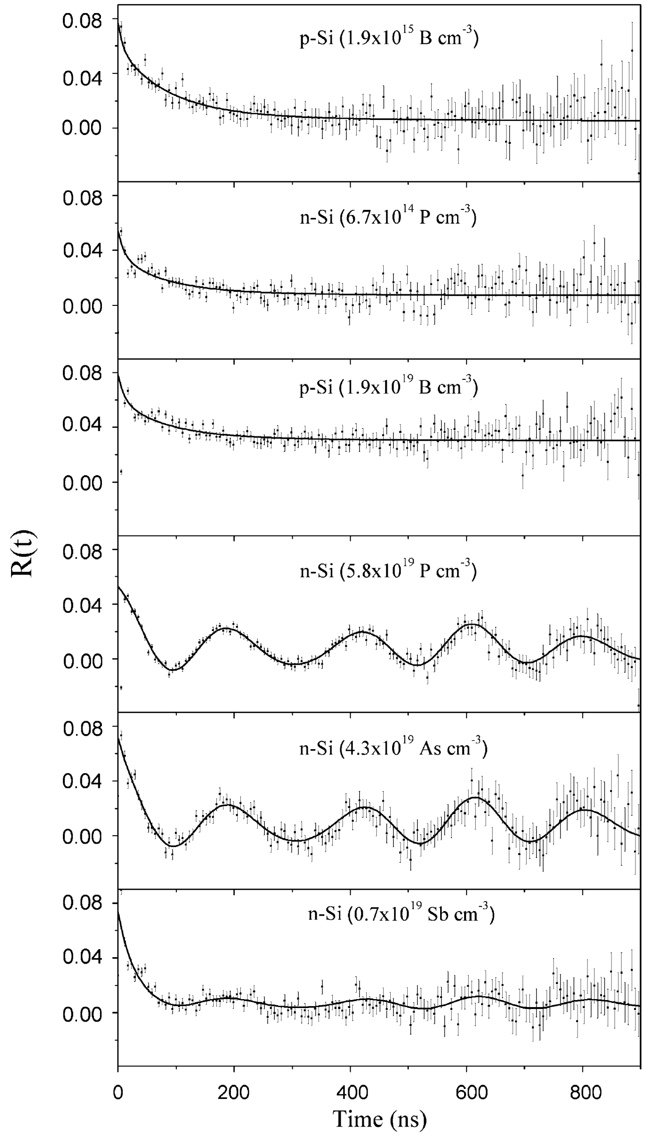

Fig. 1. PAC time spectra for various silicon samples with ^{100}Pd/Rh probe measured at room temperature. All samples were annealed at 250 °C after recoil implantation of the probe.

PAC measurements were carried out on the as-implanted film and after subsequent furnace annealing at different temperatures. The least-squares fitted time spectra $R(t)$, measured at room temperature for various samples of silicon are shown in Fig. 1. Fig. 1 demonstrates that the defect-specific EFG is present only in the highly doped n-type silicon samples which is characterized by an interaction frequency of $\nu_Q = 13.1(2)\,\mathrm{MHz}$ with an axially symmetric EFG oriented along ⟨1 1 1⟩ direction. The orientation of the principal component of the EFG tensor is confirmed by acquiring PAC time spectra with detectors positioned along ⟨1 0 0⟩, ⟨1 1 0⟩ and ⟨1 1 1⟩ lattice direction of the sample. The modulation pattern in each spectrum is consistent with ⟨1 1 1⟩ orientation of the EFG. The strong similarity of PAC spectra in highly P-, As- and Sb-doped silicon (same interaction frequency and asymmetry parameter) indicates the same defect complex formation in the nearest neighbourhood of ^{100}Rh probe nuclei. As observed earlier by our group [4], furnace annealing has shown the increased probe fraction of defect complex that reaches maximum around 250 °C and then starts decreasing with increasing annealing temperatures. This fraction diminishes around 600 °C which corresponds to dissociation of the defect complex with dissociation energy of 2.5(7) eV.

One of the major tasks of PAC experiments is to identify correctly the location of the nuclear probes in the crystal lattice, giving rise to the observed time spectrum. The lattice locations of the implanted atoms depend on the dose, energy, temperature and the impurity–host atom combinations. Arguments based exclusively on the consideration of charges and radii of host and probe atoms do not always provide unambiguous information about the probe site location. In the past, it has been realized that there are some properties and processes which determine the final location of the implanted atoms in semiconducting materials: size effects, chemical effects, impurity–vacancy complex formation and annealing effects. The observed unique interaction frequency could be assigned to the

Pd–defect or Pd–dopant pairs. In Si, pairs containing indium probe nuclei (^{111}In/Cd) and group V donors (P, As and Sb) are characterized by $\nu_Q = 179$, 229 and 271 MHz, respectively for P, As and Sb dopants with axially symmetric EFG oriented along ⟨1 1 1⟩ direction [1]. These pairs were found to have the structure of a dumbell consisting of the substitutional In probe and a group V atom on a nearest-neighbour lattice site. Therefore, we have ruled out the possibility of Pd-dopant pairs because of different hybridization between d-shell states of Pd and 3p, 4p and 5p-shell states, respectively, of P, As and Sb, one should have observed the different interaction frequency in P-, As- and Sb-doped silicon lattice with Pd probe nuclei. To further test this hypothesis, additional PAC measurements were performed on phosphorus-doped silicon samples as a function of P concentration. The measured room temperature PAC spectra are shown in Fig. 2 along with their respective Fourier transforms. The visual inspection of the spectra clearly indicates the increased probe fraction with same hyperfine parameters (i.e. $\nu_Q = 13.1$ MHz, $\eta = 0$ and EFG orientation along ⟨1 1 1⟩) as observed for P-, As- and Sb-doped samples and there is no evidence of the formation of Pd–dopant pairs or Pd–dopant clusters.

We attribute our results in highly n-type silicon to the formation of $\mathrm{Pd_{Si}}$–$\mathrm{V_{Si}}$ complex. These results are supported by the fact that highly doped n-type silicon is rich in vacancies [5], which are highly mobile at room temperature, forming divacancies or complexes with impurities. Moreover, the dopant concentration dependence of probe fraction indicates the Fermi level dependent trapping process. We exclude the possibility of pairing of negatively charged vacancies (dominant in n-type) with acceptor palladium due to Coulomb repulsion which contradicts previous studies of a Pd acceptor state in n-type Si but is consistent with the complete absence of Pd–donor pair as observed in the present measurements. Thus, we can infer that the observed $\mathrm{Pd_{Si}}$–$\mathrm{V_{Si}}$ pair must be either $\mathrm{Pd^+}$–$\mathrm{V^-}$ or $\mathrm{Pd^0}$–$\mathrm{V^-}$. The observed symmetric EFG is compatible with the structure of dumbell consisting of substitutional palladium probe and silicon vacancy on a nearest neighbour lattice site. In such a complex the orientation of principal component of EFG is along the bond centre, i.e. ⟨1 1 1⟩, and asymmetry is zero, consistent with the observations. The lower probe fraction in Sb-doped sample may be due to the fact that the Sb concentration is lower than P- and As-doped silicon that potentially yields a lesser fraction of observed palladium related defect complex.

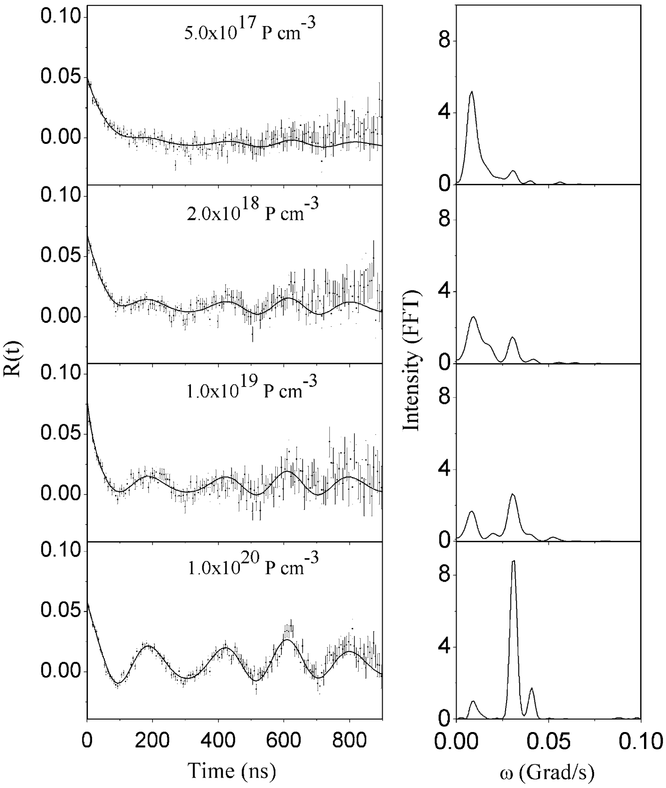

Fig. 2. PAC time spectra as a function of phosphorus concentration measured at room temperature with ^{100}Pd/Rh probe. All samples were annealed at 250 °C after recoil implantation of the probe.

Corresponding to the quadrupole interaction frequency of 13.1 MHz, the observed EFG at room temperature is $V_{zz} = 3.58 \times 10^{21}\ \mathrm{V/m^2}$. In order to investigate the origin of observed EFG, we have made calculations based upon density functional theory in the local density approximation [6]. The formation of the Rh–V complex after the decay of a Pd–V configuration is expected if the occupation of the electronic orbital corresponding to the defect complex is not influenced by the radioactive decay. Therefore, the silicon crystal lattice is simulated by a supercell containing a Rh–V pair. The calculations have also been made for Rh–V pair with one extra electron. For the present calculations, Rh–V pair and six nearest-neighbours silicon atoms were allowed to relax until the forces on all the atoms were less than 1 mRy/a.u. The three silicon atoms originally situated 2.35 Å apart from the Rh atoms moved to a closer distance of 2.29 Å while the opposite layer, originally 3.84 Å apart from the Rh atom approached to 3.77 Å. Thus the silicon atoms are pushed towards the Rh impurity while the Rh itself is moved only slightly into the vacancy (about 0.01 Å). In these simulations only the displacements allowed by symmetry of the space group were included. The density of states spectra has not shown the difference between the normal case and the one with one extra electron. In contrast, the EFG values are considerably different: $+4.76 \times 10^{21}\ \mathrm{V/m^2}$ (normal case) and $+6.04 \times 10^{21}\ \mathrm{V/m^2}$ (with an extra electron). The observed EFG with PAC technique is very close to the calculations made for Rh–V pair; we attribute our PAC results to the formation of Pd–V pair that decays to Rh–V pair in the crystal lattice of highly doped n-type silicon.

4. Conclusions

The PAC experiment has revealed that doping of silicon with Pd and dopants such as P, As, Sb and B does not lead to a formation of Pd–dopant pairs but, instead, a formation of Pd_{Si}–V_{Si} pairs only in highly doped n-type silicon irrespective of n-type dopant. The present results have been explained, and are consistent with ab initio calculations, by the formation of dumbell structure with substitutional palladium and silicon vacancy as nearest neighbour in the silicon lattice.

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