Pd-vacancy complex in Si identified with the perturbed angular correlation technique

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A Pd-vacancy (Pd-V^-) complex in Si has been identified with the perturbed angular correlation technique using the radioactive ^{100}Pd probe produced by recoil implantation. The fraction of Pd probes in the complex has been determined as a function of dopant type (B, P, As, and Sb), dopant concentration (10^{15}–6×10^{19} cm^{-3}) and annealing temperature (21–500 °C). The Pd-V^- complex, with a unique interaction frequency of 13.1(2) MHz, was observed only in n^+-Si with a maximum relative fraction of ~52% achieved between 200–300 °C while a broad distribution of interaction frequencies was apparent in *n*-, *p*-, and p^+-Si. Annealing beyond 300 °C yielded a reduction in the Pd-V^- fraction with a dissociation energy of 2.5(7) eV. Density functional theory calculations of the electric field gradient for the given defect configuration were consistent with a measured value of 3.58×10^{21} V/m^2.

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Introducing transition metals in Si can yield deep levels in the band gap that modify the electrical properties of the material. For example, Pd has been utilized to alter the carrier lifetime in switching diodes[1] and such Pd centers have previously been studied with deep-level transient spectroscopy (DLTS)[2] and electron paramagnetic resonance.[3] DLTS measurements demonstrated that Pd forms substitutional donor states in *p*-type Si and acceptor states in *n*-type Si.[4] The latter can be off-site with C_{2v} symmetry and transform to on-site with T_d symmetry, where the electronic configuration of both can be viewed as $4d^{10}+V^-$ (where V^- denotes a negatively charged Si vacancy) using with the "vacancy model" of Watkins.[5] For the current investigation, a Pd-defect complex in n^+-Si has been identified with the perturbed angular correlation (PAC) technique. This analytical method is sensitive to the local atomic environment surrounding the radioactive probe, enabling us to differentiate between various possible probe-defect configurations. Unlike DLTS, PAC measurements are not restricted to a limited dopant concentration range and are equally possible in undoped or highly doped material, as we and others have previously demonstrated with the common radioactive ^{111}In probe in both Si (see Ref. 6) and Ge.[7] In contrast, difficulties in obtaining and using the radioactive ^{100}Pd probe have restricted its usage in the study of semiconductor materials. For the current investigation, we have also developed a reliable and efficient way of producing and implanting ^{100}Pd.

PAC measurements necessitate a radioactive probe that decays via a γ-γ cascade. The hyperfine interaction between an electric field gradient (EFG) at the probe site and the nuclear electric quadrupole moment of the intermediate nuclear state perturbs the angular correlation of the two γ-rays. The EFG is the second derivative of the electrostatic potential at the probe site and cubic symmetry about a substitutional probe does *not* yield an EFG. The latter results from noncubic symmetry due to impurities, defects, and/or a noncubic lattice. In the intermediate state, the nuclear spin precesses with a frequency ν_Q proportional to the electric field gradient V_{zz} and the nuclear electric quadrupole moment Q, where $\nu_Q=|eV_{zz}Q/h|$. The angular correlation of the two γ rays is measured by recording time coincidence spectra from which the magnitude, direction, and symmetry of the EFG can be determined. Further details of the PAC technique can be found in Refs. 6–8.

Czochralski-Si wafers of (100) orientation and doped with B, P, As, or Sb were recoil implanted with radioactive ^{100}Pd probes (which decay to ^{100}Rh with a half-life of 3.63 days). The probe nuclei were produced with the nuclear reaction ^{92}Zr(^{12}C,4*n*)^{100}Pd using a 70 MeV ^{12}C beam incident on a ^{92}Zr foil of thickness ~2.5 μm. The Si samples were positioned behind the foil and off the transmitted ^{12}C beam axis (as shown in Ref. 9) subtending scattering angles of ~2°–30°. The angular distribution of recoiled ^{100}Pd was broader than that of scattered ^{12}C and thus enabled the efficient collection of ^{100}Pd without ^{12}C contamination. To further reduce the possibility of ^{12}C-related artifacts, the substrates were mechanically ground before recoil implantation to a thickness of ~50 μm followed by annealing in Ar for 30 min at 900 °C to remove residual strain or defects from the grinding process. The thinned substrates were then of lesser thickness than the projected range (~70 μm) of 70 MeV ^{12}C in Si calculated by SRIM.[10] (Although we estimate ~10^{14} cm^{-2} ^{12}C was incident on the samples, the vast majority of scattered C atoms simply passed through the thinned substrates. Furthermore, subsequent measurements using bulk samples of thickness ~550 μm showed no evidence of Pd—C interaction). The ^{100}Pd dose recoil implanted in the substrates was ~10^{12} cm^{-2} with an energy range of 0–8 MeV yielding a concentration of ~3×10^{15} cm^{-3} over depths of 0–3 μm. Samples were subsequently annealed in N_2 for 30 min at 21–500 °C. No loss of

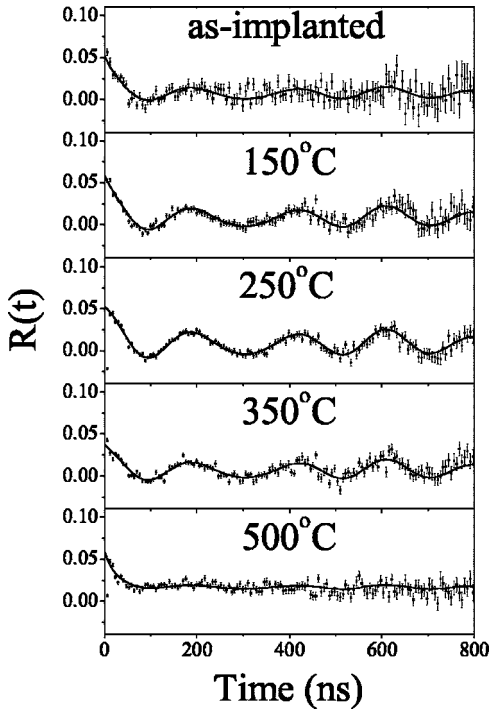

FIG. 1. PAC spectra for radioactive ^{100}Pd probes in n^+-Si (5.8×10^{19} P cm^{-3}) as a function of annealing temperature. Solid lines are fits to experimental data.

Pd was apparent over this temperature range.

PAC measurements were performed at room temperature with a co-planar array of four BaF_2 detectors positioned at 90° intervals with a ⟨100⟩ Si axis oriented toward a start detector. The ratio function $R(t)$ was formed from the measured coincidence spectra to eliminate the effects of exponential decay. The former were least-squares fitted using a three-site model comprised of: (*i*) f_1, an unperturbed Pd probe experiencing no EFG on a substitutional Si site, (*ii*) f_2, a perturbed Pd probe experiencing a well-defined and unique EFG, and (*iii*) f_3, a perturbed Pd probe experiencing a weak EFG resulting in an exponential decay of the amplitude. Figure 1 shows $R(t)$ spectra as a function of annealing temperature for n^+-Si (5.8×10^{19} P cm^{-3}). Fourier analysis demonstrated that the unique frequency apparent at $\leqslant$350 °C was 13.1(2) MHz with a frequency distribution of 0.4 MHz. The EFG was aligned along and symmetric about the ⟨111⟩ Si axis, as verified with a series of measurements varying the angular orientation of the sample with respect to the detectors. The ⟨111⟩ axis is a bond direction suggesting the source of the EFG could be located in a nearest-neighbor or interstitial position.

For the same sample, Fig. 2 shows the relative fraction of the Pd probe sites again as a function of annealing temperature. The unperturbed and weakly perturbed fractions (f_1 and f_3) are correlated and thus only their sum is shown. The weakly perturbed site was fit with a zero interaction frequency having a Lorentzian distribution of 10–30 MHz. The absence of a unique interaction frequency for f_3 eliminates the possibility that this fraction of the Pd probes form a unique defect configuration with, for example, a self-interstitial or vacancy. The probes most likely occupy sites of

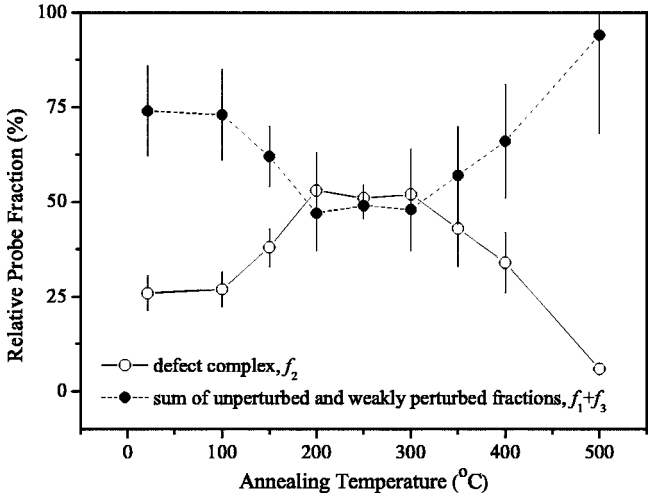

FIG. 2. Relative probe fraction in n^+-Si (5.8×10^{19} P cm^{-3}) as a function of annealing temperature. Lines are a guide to the eye.

cubic symmetry but are perturbed by the presence of recoil-implantation-induced disorder at distances beyond the first-nearest-neighbor shell. This diffuse, distant disorder yields the weak, nonunique EFG associated with the weakly perturbed fraction f_3.

The maximum relative fraction of Pd probes experiencing the unique 13.1 MHz interaction frequency (f_2) was ~52% following annealing between 200 and 300 °C. The relative fraction decreased for temperatures above 300 °C, while concomitantly, the sum of the unperturbed and weakly perturbed sites increased as consistent with the conversion from one configuration to either of the other two. The dissociation energy associated with the reduction of the 13.1 MHz Pd complex was 2.5(7) eV (as calculated following Wahl *et al.*[11]) and is similar to that reported for the divacancy in Si.[12,13]

Figure 3 shows the relative fraction of Pd probes experiencing the 13.1 MHz interaction frequency as functions of annealing temperature, dopant type and dopant concentra-

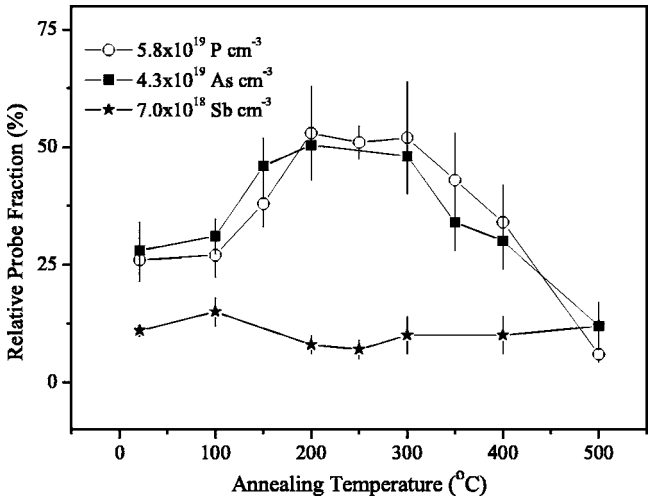

FIG. 3. Fraction of radioactive ^{100}Pd probes with 13.1 MHz interaction frequency as functions of annealing temperature, dopant type, and dopant concentration. Lines are a guide to the eye.

tion. The unique interaction frequency was *not* apparent in *n*- and *p*-type standards (6.7×10^{14} P cm^{-3} and 1.9×10^{15} B cm^{-3}, respectively) or p^+-Si (8.4×10^{19} B cm^{-3}). (For these materials, the PAC spectra were dominated by the weakly perturbed fraction, requiring only the f_1 and f_3 sites for fitting.) In n^+-Si, the value of the interaction frequency (13.1 MHz) was *independent* of the dopant type (P, As, and Sb), although the relative fraction of Pd probes experiencing such a frequency was *dependent* on the dopant concentration. For example, the measured relative fractions were near equal in P- and As-doped material (5.8×10^{19} P cm^{-3} and 4.3×10^{19} As cm^{-3}, respectively) over the entire annealing temperature range, yet were lower when the dopant concentration was reduced in Sb-doped material (0.7×10^{19} Sb cm^{-3}).

We now speculate as to the source of the 13.1 MHz interaction frequency in n^+-Si. Others have reported DLTS measurements of a Pd acceptor state in *n*-Si ($\sim3\times10^{14}$ P cm^{-3}, Ref. 4) and thus Coulombic attraction between Pd acceptors and ionized donors should enable Pd-donor pairing. However, we note that the 13.1 MHz interaction frequency identified in the current investigation with PAC was *not* present in *n*-type material with a donor concentration similar to that used for the DLTS measurements. Furthermore, we can *exclude* Pd-donor pairing given the measured interaction frequency was *independent* of the dopant type. With increasing dopant mass, the hybridization of the Pd *d*-shell states with the 3*p*-, 4*p*-, and 5*p*-shell states of P, As, and Sb, respectively, should yield different interaction frequencies. For example, Wichert and Swanson[6] reported interaction frequencies of 179, 229, and 271 MHz for, respectively, In—P, In—As, and In—Sb pairing in Si. A common interaction frequency as measured in the current investigation suggests the EFG at the probe site does not directly result from the dopant but instead from a defect configuration that is common to n^+-Si for all three dopants. The observed temperature dependence—the relative fraction was a maximum at 200–300 °C—further supports a defect-related complex given the much greater diffusivity of the intrinsic defects relative to the atomic constituents.

As noted previously, Pd acceptors in *n*-Si can transform from off-site with C_{2v} symmetry (perturbed) to on-site with T_d symmetry (unperturbed) as determined with DLTS.[2] The reported temperature dependence of the transformation is similar to that of the 13.1 MHz fraction shown in the present study. However, we again exclude such a configuration given that the off-site orientation determined with DLTS was along the ⟨100⟩ axis, while our PAC measurements show the EFG was symmetric about the ⟨111⟩ axis. The latter suggests a "dumbbell" model in which a substitutional Pd probe is bonded to a defect in the nearest-neighbor position. An alternative interpretation is a Pd probe in the center of a split vacancy similar to that suggested for Sn-vacancy[14] and Cd-vacancy[15] complexes in Si. PAC is unable to distinguish between these two models.

The donor concentration dependence of the fraction of probes experiencing the 13.1 MHz interaction frequency is consistent with a Fermi-level dependence, suggesting the related defect is charged. Nakabayashi *et al.*[16] have shown that V^- is the most abundant charged defect in n^+-Si ($\sim3\times10^{19}$ P cm^{-3} and $\sim4\times10^{19}$ As cm^{-3}) and [V^-] increases linearly with donor concentration. Our 13.1 MHz fraction increased in similar fashion and, having previously excluded other potential configurations, we now assign a configuration of Pd-V^- to our complex. To support such an assignment, density functional theory (DFT) calculations based upon the local density approximation[17] were performed for a rhombohedral supercell (with $R3m$ space group symmetry) containing a relaxed Rh-V^- complex in a Si lattice. (The decay of the radioactive Pd probe to Rh necessarily converts the Pd -V^- complex to Rh-V^-. To observe the Rh-based complex, it *must* first have been formed about the Pd probe.) For the present calculations, the Rh-V^- complex and six nearest-neighbor Si atoms were relaxed until the forces on all atoms were less than 1 mRy/a.u. During this process, the point group symmetry for each atom was kept fixed and no spin-polarized calculations were performed. The three Si atoms originally 2.35 Å from the Rh atom moved to a lesser distance of 2.29 Å, while the three Si atoms originally 3.84 Å from the Rh atom approached to 3.77 Å. The six Si atoms thus contracted toward the Rh atom, while Rh itself moved only slightly (~0.01 Å) toward the vacancy. In these simulations, only the displacements allowed by symmetry of the space group were included. The calculated EFG at the Rh probe site was 4.76×10^{21} V/m^2, similar to our measured value of $3.58\pm0.19\times10^{21}$ V/m^2 (taking $Q=0.151\pm0.008$ b).[18]

We can also speculate as to the charge state of the radioactive ^{100}Pd probe. Pairing with a negatively charged vacancy effectively eliminates a negative Pd charge state due to Coulomb repulsion. This contradicts previous studies of a Pd acceptor state[4] in *n*-Si, but is consistent with the complete lack of Pd-donor pairing observable in this report. A neutral Pd charge state would suggest Pd-V^- pairing is governed by an elastic interaction, potentially as a mechanism to relieve strain about an oversized Pd atom in a Si lattice. (The electronic configuration of the complex is thus $4d^{10}+V^-$.) A positive Pd charge state would infer Pd-V^- pairing is governed by a Coulombic interaction, and, as above, is consistent with the absence of Pd-donor pairing.

In summary, the PAC technique has been utilized to identify a Pd-V^- complex in n^+-Si. Our assignment of a Pd-V^- configuration is based on the annealing temperature, donor type, donor concentration, and Fermi-level dependencies, and is further supported by DFT calculations. Finally, we suggest the Pd charge state in the Pd-V^- complex is either neutral or positive in n^+-Si.

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