Correlation of residual impurity concentration and acceptor electron paramagnetic resonance linewidth in isotopically engineered Si

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Electron paramagnetic resonance (EPR) experiments on boron acceptors in isotopically engineered ^{28}Si samples with different degrees of chemical and isotopic purity are reported. The strong suppression of isotope-induced broadening effects in this material allows a direct observation of the linear correlation between the width of the inter-subband $\Delta m = 1$ EPR line and the concentrations of carbon, oxygen, and boron point defects down to a total concentration of $\approx 2 \times 10^{15}$ cm^{-3}. When the impurity level is decreased further, the linewidth does not fall below 2.3 ± 0.2 mT, for which we discuss possible origins. © *2011 American Institute of Physics*. [doi:10.1063/1.3606548]

The combination of the *p*-type character of the orbitals forming the top of the valence band in semiconductors and the spin-orbit coupling leads to a fourfold degeneracy of the valence band edge in silicon,[1] as well as of the valence band-related ground states of shallow substitutional acceptors such as boron. This degeneracy is lifted when the crystal symmetry is broken. For example, a strong and homogeneous external magnetic field, as used in electron paramagnetic resonance (EPR) experiments, splits the ground state into four Zeeman levels. Between these levels, resonant transitions can be induced by the combined action of oscillating electric and magnetic fields.[2–4] The spin-orbit coupling also makes these valence band-derived states very susceptible to changes in the wave function caused by external and internal stress. A random distribution of point defect-induced strain can lead to a splitting of the acceptor ground state even in the absence of external symmetry-lowering perturbations and varying in magnitude at individual acceptors. Given a sufficient chemical purity of the Si crystal, this effect can be treated as a small perturbation of the Zeeman levels which translates into an inhomogeneous broadening of the EPR resonance lines with a Lorentzian line shape.[4,5] It has been shown for Si crystals with a natural isotope composition (^{nat}Si) and a large concentration of impurities of $\approx 10^{16} - 10^{17}$ cm^{-3} that the linewidth of the broad $\Delta m = 1$ EPR resonance line, where m is the magnetic quantum number of the effective spin 3/2 acceptor state, increases linearly with the concentration of carbon and oxygen point defects.[6] However, for lower concentrations of point defects, the effect of local strains is masked by the broadening of the EPR line due to the random spatial distribution of ^{28}Si, ^{29}Si, and ^{30}Si isotopes in ^{nat}Si (Refs. 7–10). Here, we demonstrate that in isotopically pure ^{28}Si the width of this EPR line is again governed by the internal strain fields generated by these impurities and that the linewidth can be used to quantify their concentration down to levels of 2×10^{15} cm^{-3}.

For this study, we have used six ^{28}Si samples from charges 7, 9, and 10 of the Avogadro project.[11–13] All crystals were float-zone grown and received several passes in vacuum and highly pure argon. To remove surface damage resulting from the cutting, the samples were etched in a 10/1 mixture of nitric and hydrofluoric acid. All EPR spectra shown were recorded at 2.2 ± 0.3 K using a commercial X-band EPR spectrometer.[9,10] In Fig. 1, we compare the

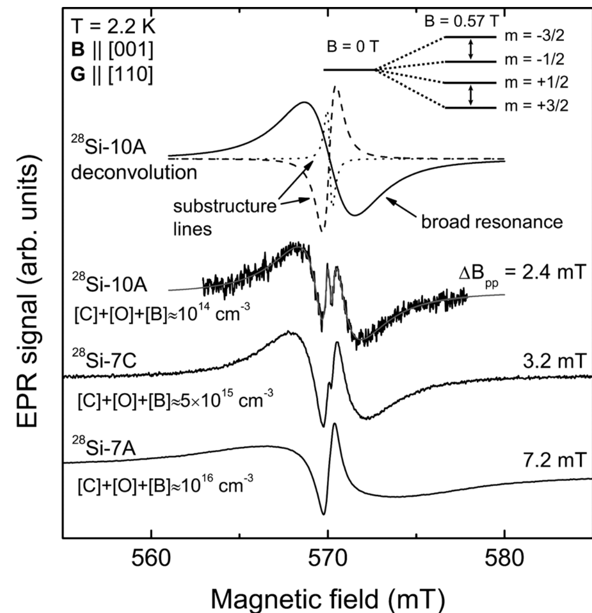

FIG. 1. Normalized EPR spectra of the $\Delta m = 1$ resonance with $m = \pm 1/2 \leftrightarrow m = \pm 3/2$ (see inset) of three ^{28}Si samples. The peak-to-peak linewidths ΔB_{pp} given are those of the broad resonance as determined by numerical fitting. For the spectrum of sample ^{28}Si-10A the result of a simulation taking into account the derivatives of three Lorentzian lines is shown as grey curve as well as the deconvolution of the fitted line into its three Lorentzian components.

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EPR resonance assigned to the $\Delta m = 1$ transitions $m = -3/2 \leftrightarrow m = -1/2$ and $m = +3/2 \leftrightarrow m = +1/2$, as shown in the inset of Fig. 1, exemplarily for three different ^{28}Si samples. The energy splitings for these inter-subband transitions between light hole-like and heavy hole-like states are directly influenced by strain fields in first order perturbation theory, which is not the case for the $m = -1/2 \leftrightarrow m = +1/2$ resonance representing an intra-subband transition between two light hole-like states.[4,10] The broad resonances between light hole and heavy hole-like states are superimposed by narrow substructure lines. For sample ^{28}Si-7A showing the largest overall linewidth, only a single substructure line with negative sign compared to the broad resonance is observed. This structure originates from a dynamic double-excitation effect in a subensemble of acceptors that show a symmetric level splitting.[9] In the spectra of the samples with the smallest linewidth, an additional, even narrower, substructure line arises, which shows a positive sign. The origin of the latter substructure could not be clarified so far and shall not be discussed further here.

To extract the linewidth of the underlying broad resonance which is the measure for the concentration of point defects, we have fitted the resonances by the derivatives of three Lorentzian lines, as shown in Fig. 1 for sample ^{28}Si-10A. The peak-to-peak linewidths ΔB_{pp} given in Fig. 1 represent the linewidth of the broadest resonance obtained from the simulations of the individual spectra. The broad resonances of all samples show a slight asymmetry which is presumably induced by a very small external strain in combination with the thermal spin polarization leading to an unequal contribution of the two transitions $m = -3/2 \leftrightarrow m = -1/2$ and $m = +3/2 \leftrightarrow m = +1/2$ to the resonance line. In the simulations, this asymmetry is accounted for phenomenologically by small shifts of the resonance fields of the two substructure lines with respect to the broad resonance to lower magnetic fields by $\approx$0.02–0.09 mT. Note that these shifts are significantly smaller than ΔB_{pp} and do not influence the value of the latter.

In Fig. 2(a), we plot ΔB_{pp} of the broad Lorentzian resonance as a function of the sum of the concentrations of carbon, oxygen, and boron point defects [C] + [O] + [B]. For the ^{28}Si samples measured here, these concentrations were determined by local vibrational mode infrared absorption spectroscopy and photoluminescence measurements[14] with an uncertainty indicated by the horizontal error bars. The concentration of all other contaminants including nitrogen in our samples is much lower than [C] + [O] + [B]. Vertical error bars, which have a visible size only for two data points, represent the uncertainty of the linewidths determined as described above. For ΔB_{pp} of ^{nat}Si in Fig. 2(a), we plot the values published by Neubrand of the Lorentzian fraction of the Voigt line he used to phenomenologically describe the observed resonance line width.[6] As noted by Neubrand, ΔB_{pp} of the Lorentzian is proportional to the impurity concentration. The dashed line indicating a linear relationship shows that this is also true for the isotopically pure ^{28}Si crystals and that the linearity holds to significantly lower concentrations of [C] + [O] + [B] $\approx 2 \times 10^{15}$ cm^{-3}, extending the previously observed range by about one order of magnitude. The dependence of the linewidth on the defect concentration is proportional to the average elastic strength of the different point defects. Applying the isotropic continuum approximation as described in Ref. 6, the average elastic strength corresponding to the dashed line in Fig. 2 is $A = 2.1$ Å^3. This value is a more than a factor of 2 larger than the value calculated from changes of the lattice constant for samples with known concentrations of point defects.[6] One possible explanation for this is that the isotropic continuum approach is not a good approximation for Si (Ref. 6). However, the accuracy with which the data obtained from ^{28}Si extend the linear dependence of the Lorentzian linewidth contribution in ^{nat}Si to lower concentrations of point defects is impressive, and our data show that isotopic purification allows for the measurement of much lower point defect concentrations via EPR.

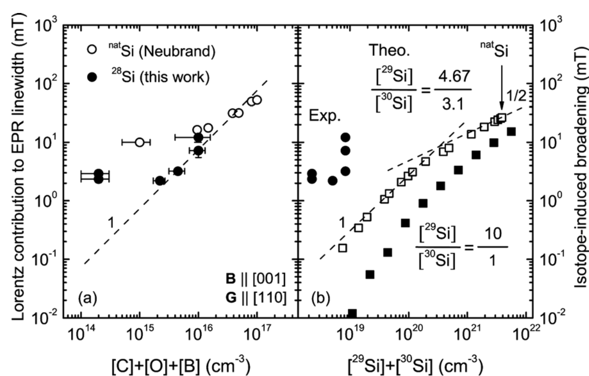

FIG. 2. (a) Linewidth of the inter-subband $\Delta m = 1$ resonance as a function of [C] + [O] + [B]. Full dots show the data measured in this work on isotopically purified ^{28}Si samples, open dots the width of the Lorentzian contribution to the overall linewidth reported on ^{nat}Si samples in Ref. 6. (b) Expected broadening due to residual ^{29}Si and ^{30}Si isotopes plotted as a function of [^{29}Si] + [^{30}Si] for different ratios of [^{29}Si] to [^{30}Si] using the model described in Ref. 10. The dashed lines are guides to the eye indicating linear and square-root dependencies.

The ^{nat}Si data show a saturation at a minimum impurity-related Lorentzian linewidth contribution of approximately 10 mT. This threshold value is an artifact of the Voigt model that does not describe the line shape of the $\Delta m = 1$ resonance in ^{nat}Si appropriately in the limit of low point defect concentrations.[10] The limiting value of the EPR linewidth of $\approx$2.3 mT observed for ^{28}Si could have several possible origins:

(i) The observation of the substructure lines on the broad resonance can only occur if a distribution of Zeeman level splitings corresponding to an inhomogeneous broadening is the origin of the broad resonance.[9,10] This excludes that homogeneous broadening determined by spin relaxation and decoherence at the temperature of the experiment determines the linewidth.

(ii) As in the case of ^{nat}Si discussed above, the linewidth might be limited by the residual ^{29}Si and ^{30}Si isotopes. Based on the model developed in Ref. 10, the expected isotope-induced broadening is plotted as a function of the sum of the residual ^{29}Si and ^{30}Si concentrations in Fig. 2(b) under two different assumptions: for [^{29}Si]: [^{30}Si] = 4.67:3.1 corresponding to the ratio of the concentrations of these isotopes in ^{nat}Si (open squares), and for [^{29}Si]:[^{30}Si] = 10:1 as typical for the isotopic purification process.[11] For the latter, only the $m = +3/2 \leftrightarrow m = +1/2$ resonance was used to extract the linewidth, as the two $\Delta m = 1$ transitions show a splitting that

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becomes significant for the small linewidths predicted in this case.[10] For crystals of very high isotopic purity with $[^{29}\mathrm{Si}]+[^{30}\mathrm{Si}] \lesssim 10^{20}$ cm^{-3} corresponding to a ^{28}Si content >99.8%, the isotope effect leads to an inhomogeneous line broadening proportional to $[^{29}\mathrm{Si}]+[^{30}\mathrm{Si}]$ [see Fig. 2(b)] and a corresponding Lorentzian line shape. As for the C, O, and B impurity-induced strain in our samples discussed above, such a behavior is typical for point defect-induced broadenings where the change of the transition energy due to the defects can be treated by first order non-degenerate perturbation theory.[5] For larger $[^{29}\mathrm{Si}]+[^{30}\mathrm{Si}]$, the perturbation of the acceptor due to the presence of the different Si isotopes leads to a significant mixing of the Zeeman states, which is also responsible for the asymmetry of the $m=-1/2 \leftrightarrow m=+1/2$ resonance observed in $^{\mathrm{nat}}$Si (Ref. 10). In this regime, as can be seen in Fig. 2(b), the isotope-induced broadening causes the linewidth to increase proportional to $([^{29}\mathrm{Si}]+[^{30}\mathrm{Si}])^{1/2}$ and the line shape to become Gaussian, a behavior which, for large concentrations of point defects, is also dictated by the central limit theorem.[1] A similar transition between these two inhomogeneous broadening regimes as a function of $[^{29}\mathrm{Si}]$ has also been reported for P donor electron spin resonance, where the inhomogeneous broadening is caused by the hyperfine interaction of the donor electrons with ^{29}Si nuclear spins.[15] At least the linear dependence of the linewidth on the concentration of ^{29}Si and ^{73}Ge has also been observed for the hyperfine-induced broadening of dangling-bond resonances in hydrogenated amorphous Si and amorphous Ge, respectively.[16,17] However, as can be seen, an isotope-induced broadening of 2.3 mT would only be expected for Si crystals with an isotopic purity of less than 99.8% ^{28}Si ($[^{29}\mathrm{Si}]+[^{30}\mathrm{Si}] > 10^{20}$ cm^{-3}), which can be ruled out for all enriched samples studied here.

(iii) Intrinsic point defects such as vacancies and self-interstitials could also be responsible for the observed residual broadening, if present at a sufficiently large concentration. Calculations of the formation energies of Si vacancies employing density-functional theory yield formation energies in the range between 3 and 5 eV (Ref. 18). Ab-initio calculations on several of Si self-interstitial configurations similarly obtain formation energies between 4 and 4.5 eV (Ref. 19). These values indicate that the equilibrium concentration of intrinsic point defects should be negligible ($\ll 10^{10}$ cm^{-3}), even at temperatures where the Si crystals are grown. Also dislocations can generate internal strain fields inducing a broadening of acceptor EPR lines. However, a dislocation-induced broadening is expected to lead to a nearly Gaussian line shape.[5] In addition, all crystals investigated show a very low dislocation density of much below 10 cm^{-2}.

(iv) Apart from perturbations within the crystal, also external perturbations could be responsible for the linewidth limit observed. For stress along the [110] crystallographic axis, it has been shown that the broad $\Delta m=1$ resonance splits into two lines corresponding to the $m=-3/2 \leftrightarrow m=-1/2$ and $m=+3/2 \leftrightarrow m=+1/2$ resonances with a splitting of 3.9 mT/(N cm^{-2}).[4] We have taken care to mount the samples free of external stress, keeping them in place mainly by their own weight oriented such that the gravitational force $\mathbf{G}||[110]$. The mass of our EPR samples lies between 0.05 and 0.1 g. For an area of $\approx$0.03 cm^2 on which the sample resides during measurement, the maximum splitting expected for the acceptors in the lowest part of the sample due its weight is $\approx$0.1 mT. While this number is noteworthy and demonstrates the extremely large sensitivity of acceptor states to external strain, it, however, is more than one order of magnitude too small to account for the residual broadening of 2.3 mT. However, if the EPR linewidth in the charge 10 samples was limited by their characteristically high nominal ^{28}Si concentration and small [C] + [O] + [B], stress induced by the weight of the sample would become a relevant broadening mechanism. In this case, experiments removing the effect of gravitation would become interesting.

(v) Finally, the broadening could also be induced by residual surface strain as already pointed out by Neubrand, who observed an increase of the linewidth of the broad resonance to 60 mT after slight grinding of his samples.[6] Although we took care to etch our samples to remove surface damage caused by cutting, it cannot be guaranteed that the treatment has been sufficient. This attribution is supported by the fact that the smallest linewidth is observed for a sample with a particularly high volume-to-surface ratio although this sample does not show the highest chemical purity (cf., Fig. 2). For the two samples with the highest chemical purity, a significantly smaller linewidth is measured for the sample with an $\approx$40% higher volume-to-surface ratio. These observations might indicate a strong effect of the surface on the EPR linewidth under conditions of very high chemical and isotopic purity.

In summary, we have shown that the $\Delta m=1$ inter-subband EPR line of B in highly enriched ^{28}Si shows an inhomogeneous Lorentzian broadening proportional to [C] + [O] + [B] down to $\approx 2 \times 10^{15}$ cm^{-3}. For samples with $<10^{15}$ cm^{-3} point defects, we find a linewidth limit of $\approx$2.3 mT for which we have discussed different possible explanations. Further EPR experiments on samples with different volume-to-surface ratio cut from the same crystal as well as after different surface treatments could clarify the effect of the surface on the broadening observed in the limit of chemically and isotopically highly pure Si crystals.

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