Investigation on the Effect of Charge Carriers in Chemical Shift Anisotropy of Si Single Crystal

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Abstract. The Chemical Shift Anisotropy (CSA) of single crystalline silicon (Si) was investigated using ²⁹Si static NMR for commercially procured p-type and n-type silicon. The observed CSA has been distributed between -80 ppm to -90 ppm for n-type and p-type Si. The NMR parameters such as Isotropic Chemical Shift (δiso), Chemical Shift Anisotropy tensor (Δδ) and the asymmetry parameter (η) of the CSA were extracted by using DMFIT with the CSA-static model. The Δδ and η are found to be -1.73 ppm and 0.3 ppm respectively for the n-type and the asymmetry parameter of the CSA was found one order different from p-type material. The changes observed in CSA pattern and spin-lattice relaxation (T₁) time are ascribed to strength (mobility) of the shallow donor level and shallow acceptor level effects in the Fermi contact term.

1. Introduction
Silicon based materials are very effective in energy storage applications, photonics and photovoltaic cells with high efficiencies and high densities¹–⁸. It has been reported recently that microstructure and electronic properties probes the detection of nitrogen impurities in phosphorous doped silicon⁹. The solid state NMR spectroscopy were sensitive at the subatomic scale as they influence dramatically the NMR parameter with respect to their chemical and structural nature¹⁰. Most of the parameters in NMR spectroscopy, are decided by the electron and nuclear interaction terms from the total Hamiltonian. For instance, the total Hamiltonian of any system is encompasse the individual Hamiltonian’s of electron (Hₑ) from the group of interacting electron, nuclear (Hₙ) from nuclear interaction with external magnetic field or Zeeman energy plus the magnetic dipolar coupling among the nuclei, and electron-nuclear (Hₑₙ) from magnetic coupling between the nucleus and the electron spin respectively¹¹. Any shift observed in NMR parameters primarily due to the electron probability from non-zero probability, which is known to be contact Knight shift or Knight shift. The quantum computation is an complimentary technique to understand the spin manipulation at the atomic level. There are some reports which has explained the chemical shielding tensor parameters of the boron phosphide nanotubes by using DFT...
technique\(^\text{12}\). In order to engineer the spin dynamics in semiconductors, which is much warranted, the study of NMR parameters are essential\(^\text{13,14}\). With this motivation the authors investigated the spin dynamics of silicon single crystals using \(^{29}\text{Si}\) NMR measurements.

2. Methods

The commercially available \(n\)-type and \(p\)-type silicon single crystals were utilized for \(^{29}\text{Si}\) static NMR studies and \(^{29}\text{Si}\) spin-lattice relaxation NMR studies. The experiments were carried out in broad-brand probe equipped with 7 mm zirconia rotor tuned at Larmor frequency of 79.495 MHz in a superconducting magnet of 9.39 T at room temperature, associated with Bruker -AVANCE DRX- 400 NMR spectrometer. The silicon possess spin \(\frac{1}{2}\) nuclei (with abundance 4.7\%), showing large spin lattice relaxation \((T_1)\) in crystalline form \((T_1= 3\ h)\). In order to study such a long \(T_1\) materials, we have adopted a initial combo-pulse such as series (50 number of pulses) of \(\pi/2\ (1.2\ \mu s)\) pulses, with a fixed recovery time delay \(\tau\) after the combo-pulses, and the actual \(\pi/2\ (90^\circ)\) pulse. In the case of spin-lattice relaxation time, the delay between the pulses were varies in order to probe the exponential behavior of magnetization. The measured chemical shifts were presented in \(ppm\), which are referenced with respect to DSS (4, 4-Dimethyl-Silapentane-1-Sulfonic acid) taken as the standard reference. The spectral simulations made with DMFIT2006\(^\text{15}\) and the measured saturation recovery of the delay time dependent change in magnetization were fitted with Topspin 2.1.

3. Research and Discussion

3.1. Spectral Studies

This present study focuses on comprehensive understanding of doping effect in semiconducting material, which is an extension work of our previous study on the effect of SHI irradiation in nitrogen doped 6H-SiC samples\(^\text{16}\). Figure 1 shows the \(^{29}\text{Si}\) static NMR spectra of \(n\)-type silicon (a) and \(p\)-type silicon (b) recorded the Larmor frequency of 79.495 MHz. The solid-black line shows the experimental chemical shift anisotropy spectra and the solid red line shows the chemical shift anisotropy simulated using DMFIT\(^\text{15}\). The NMR parameters such as, isotropic chemical shift \((\delta_{iso})\), chemical shift anisotropic tensor \((\Delta \delta)\) and the asymmetry parameter \(\eta\) of the chemical shift anisotropy were extracted by using DMFIT\(^\text{15}\) with chemical shift anisotropy static model,

\[
\sigma_{iso} = 1/3 \left( \sigma_{xx}^{PAF} + \sigma_{yy}^{PAF} + \sigma_{zz}^{PAF} \right)
\]

\[
\Delta \delta = \left( \sigma_{zz}^{PAF} - \sigma_{iso} \right)
\]

\[
\eta = \left( \sigma_{xx}^{PAF} - \sigma_{yy}^{PAF} \right)
\]

The best spectral simulations were achieved with standard deviation between 1 to 2, for both \(n\)-type and \(p\)-type silicon static spectra, by allowing the parameters to reach the best convergence. The position of the peak is dictated by the electron density around the nucleus. The electron density makes the shielding of the external magnetic field to the nucleus. If the electron density is more near to nucleus which causes effect of external magnetic as low. Then the nucleus experienced low magnetic field and the peak appear further up field (to the left) in the spectrum. If the electron density is low, the peak of the nucleus appear further downfield (to the right) in the spectrum.

In this work, the experimentally measured chemical shift anisotropy is distributed between −80 \(ppm\) to −90 \(ppm\) for both \(n\)-type and \(p\)-type silicon. However from the DMFIT simulation\(^\text{15}\), the actual isotropic chemical shifts were appeared at −83.73 \(ppm\) and −84.61 \(ppm\) for \(n\)-type \((\delta_{iso}(n-Si))\) and \(p\)-type \((\delta_{iso}(p-Si))\) respectively. The electron density around the nucleus in \(n\)-type Si is higher than the electron density in \(p\)-type due to the nitrogen doping introduce additional electronic shielding in \(n\)-Si. The observed chemical shift anisotropic tensor \(\Delta \delta\) is found to be at −1.73 \(ppm\) and −3.38 \(ppm\) for \(n\)-
type (δ_{iso}(n-Si)) and p-type (δ_{iso}(p-Si)) respectively. On the other hand, the asymmetry parameter (\(\eta\)) found to be in 0.3 ppm and 0.082 ppm for n-type (δ_{iso}(n-Si)) and p-type (δ_{iso}(p-Si)) respectively.

Table 1. DMTFT simulation of \(^{29}\text{Si}\) static NMR spectrum

| Type of doping       | Isotropic Chemical Shift (δ_{iso} in ppm) | Chemical Shift Anisotropic Tensor (\(\Delta\delta\) in ppm) | Asymmetry Parameter (\(\eta\) in ppm) | Standard deviation |
|----------------------|------------------------------------------|----------------------------------------------------------|--------------------------------------|--------------------|
| n-type silicon       | -83.73                                   | -1.73                                                    | 0.3                                  | 1.8                |
| p-type silicon       | -84.61                                   | -3.38                                                    | 0.08                                 | 1.3                |

3.2. Spin-Lattice Relaxation Studies

Figure 2 shows the spin-lattice relaxation times (\(T_1\)) for both n-type and p-type samples under static condition using saturation recovery method. A combination of initial combo pulse with fixed delay between the pulses were adopted to magnetize saturation of \(^{29}\text{Si}\) in longitudinal plane the for such a long \(T_1\) samples. The net or average magnetization (\(M_z(t)\)) for each recovery delay time \(\tau\) after the \(\pi/2\) pulse were recorded. The spin lattice relaxation time were determined using Eq.(4) by analyzing acquired recovery of magnetization as a function of saturation recovery delay time. The driven conventional form of relaxation function can be justified with magnetization recovery using the following expression,

\[
\langle M_z(t) \rangle = M_0(1 - \exp (-t/T_1))
\]

The gradual increase of \(^{29}\text{Si}\) magnetization as a function of the saturation recovery delay time (\(\tau\)) is shown in Figure 2.
The mechanism of relaxation of $^{29}$Si is mainly due to the interaction between nuclear spin and electrons, which is consistent with the mechanism explained by N.C. Halder. It has been reported that the relaxation time is a comprehensive tool to probe the effect of doping in solids as the conduction electrons readily interact directly to the fixed nuclear site. The measured spin lattice relaxation times of silicon immediately led us to estimate the effect arising from the doping or impurity atom. The fluctuation of spin state of the conduction electrons or holes will always influence the NMR spin lattice relaxation in semiconductor. The $T_1$ in semiconductor were mainly arises from the fluctuations in spin state of the conduction electrons ($n$-type) or holes ($p$-type) and has been studied in the present investigation.

In doped Si, the mobile electrons or holes that are the dominant effect in relaxation time corresponding as the electrons shielding or de-shielding nature due to nitrogen and phosphorous doping respectively. Compared to undoped silicon the value $T_1$ (3 h) is very much reduced, because of hyperfine coupling between the large electron density at the conduction band and the $^{29}$Si nuclei. From the discussion, the general factors which affect the relaxation time $T_1$ in semiconductor are the conduction electrons (depending on the doping concentration), localized paramagnetic centers, and the mechanism of transport phenomena.

An early study by Stephen Hartman reported that the relaxation of $^{29}$Si site in silicon carbide is affected by the given carrier concentration and it has been reported that the relaxation rate ($1/T_1$) was affected eight times faster in $n$-type silicon than the $p$-type silicon. The similar such magnitude of eight times faster relaxation rate is observed in $n$-type silicon than in $p$-type silicon, from this present investigation of the spin-relaxation study of $p$-type and $n$-type silicon. This is because of the spin-lattice relation is mainly affected due to the charge carriers, in our case the relaxation is affected because of the effective mass is directly proportional to the resonance frequency.

As it has been known that the resonance frequency $\vartheta = eB_0/2\pi m^*c$ of any nuclei is mainly depend on the effective mass, hence the difference observed in our experimental are due to large effective mass of for $n$-type with respect to less in $p$-type. For instance, the effective mass of electron and holes are 1.08 ($m_e^*$) and 0.56 ($m_h^* = 0.56$) respectively and hence the effect is pronounced. The observed $T_1$ is 218 for $n$-type silicon. In the present work, the relaxation time $T_1$ for $p$-type silicon is

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**Figure 2.** $^{29}$Si Magnetization evolution as a function of the saturation recovery delay ($\tau$) for (a) $n$-type silicon, (b) $p$-type silicon.
found as 1740 s. It reveals that the hyperfine interaction between the hole and the $^{29}$Si nuclei is weak compared to that between the electron and the nuclei. In order to understand further the fundamentals of conduction band electrons to electronic shielded nucleus, the theoretical calculations using Density Functional Theory (DFT) were employed. The current study clearly emphasis the effect of charge carriers in chemical shift anisotropy of solids, which brings the motivation for the futuristic study in more complex structure, such as doping in layered structures using in solid state NMR and DFT study.

4. Conclusions
The changes observed in CSA pattern and spin-lattice relaxation time are ascribed to strength (mobility) of the shallow donor level and shallow acceptor level affects in the Fermi Contact term. From the $^{29}$Si static measurement, the change in NMR parameters like $\delta_{iso}$(static), $\Delta \delta$ and $\eta$ parameters in n-type and p-type Si are discussed. The spin-lattice relaxation time in p-type Si is lower than n-type Si because of the hyperfine interaction of electrons in Si. The effect of electron nuclear interaction in n-type and p-type Si, through $^{29}$Si spin-lattice relaxation studies, are discussed.

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