Decoupling bulk and surface recombination properties in silicon by depth-dependent carrier lifetime measurements

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Muons, as a bulk probe of materials, have been used to study the depth profile of charge carrier kinetics in Si wafers by scanning the muon implantation depth. The photoexcited muon spin spectroscopy technique can optically generate excess carriers in semiconductor wafers, while muons can measure the excess carrier density. As a result, carrier recombination lifetime spectra can be obtained. The depth-dependent lifetime spectra enable us to accurately measure the bulk carrier lifetime and surface recombination velocity by fitting the spectra to a simple 1-dimensional diffusion model. Unlike other traditional lifetime spectroscopy techniques, the bulk and surface recombination properties can be readily de-convoluted in this method. Here, we have applied the technique to study silicon wafers both with and without passivation treatment, and have demonstrated that the model can correctly describe the carrier kinetics in these two cases.

Charge carrier kinetics in semiconductors is one of the most important properties in device characterization and optimization, which ultimately determines the overall device performance. Among the various parameters that describe carrier transport, the excess carrier recombination lifetime is a key figure of merit in photovoltaics applications, which governs the efficiency of solar cells. Lifetime is a key figure of merit in photovoltaics applications, which governs the efficiency of solar cells.

The depth profile of implanted positive muons in a silicon sample is created when an implanted positively charged muon mu+ captures an electron e− and forms a muonium state: Mu+ + e− → Mu− + hν. Because the muonium state is in the triplet state, the residual muon spin in the latter state will be depolarized. Based on this carrier exchange interaction, one can expect quite naturally that the induced spin relaxation rate λ will be proportional to the excess carrier density Dn. Indeed, λ can be used as a measure of Dn by obtaining a dependence of λ relative to Dn, where Dn can be calculated from a measured photon fluence and attenuation coefficient α. This procedure, in turn, allows us to calculate Dn from a measured value of λ, and therefore the carrier lifetime spectrum (CLS), ∆n(t), can be measured. Here, t is the pulse delay between muons and pump photons, as shown in Fig. 2(a). Details of the procedure are described in our previous studies.

One of the most important advantages of this technique is that the implantation depth of muons is variable, which enables us to measure the CLS at a specified depth in a wafer. The depth profile of implanted

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muons can be approximated to a Gaussian distribution with its FWHM ≈85 µm in the case of crystalline Si. The muon distribution within the sample can be considered as stationary within the spatial and temporal scale of the measurement because the diffusion constants of the Mu centers are generally in the order of $10^{-3}$ cm$^2$/s in semiconductors at RT. Using a “surface” muon beam with an energy of 4 MeV, the center of the muon distribution can be scanned between the sample surface and the maximum implantation depth, which is ≈700 µm in Si. The muon stopping position can be adjusted by placing material (called a “degrader”) in the muon beam before the sample to modify the incident beam energy. Hence, the CLS can be measured at several depths, which provides a sterial picture of the excess carrier kinetics. The set of lifetime spectra can be fitted simultaneously to a 1-dimensional (1-D) diffusion model, which numerically calculates the dynamics of excess carriers with $\tau_0$ and $S$ as fit parameters. In this way, the recombination parameters can be measured separately with good accuracy.

To demonstrate the method, a photo-$\mu$SR experiment studying Si wafers was carried out using the HiFi spectrometer at the ISIS Neutron and Muon Source at the STFC Rutherford Appleton Laboratory in the UK. A detailed discussion of this unique laser facility and associated equipment can be found elsewhere. In this experiment, 100% spin-polarized muons are incident on one side of the sample, while pump light illuminates the other side, as shown in Fig. 1(b). Here, the sample is a 2-inch diameter, 1 mm thick, float-zone grown single crystal Si wafer (intrinsic, R>10000 Ωcm, both sides chemically polished) with the <111> axis perpendicular to the surface. The sample was contained in a helium-gas purged cell, with a 100 µm thick titanium window on one side (for muon entry) and a glass window to admit light on the other side. The gas purged construction ensured that the sample temperature was kept at 290 K throughout the experiment. A small magnetic field (100 G) was applied parallel to the initial $\mu^+$ spin direction (longitudinal field, LF) for decoupling the intrinsic relaxation in “dark” $\mu$SR spectra. This relaxation may be due to trace impurities in the sample or field inhomogeneity of the instrument, while nuclear moments of Si$^{29}$, an isotope with spin $\frac{1}{2}$, magnetic moment of -0.555 (in nuclear magnetons), and 4.7% natural abundance, can also contribute. Aluminum foils were used as a degrader for decelerating muons and adjusting the implantation depth. Note that muons stopped in the Al degrader or Ti window (especially for position 5) form diamagnetic centers and only give a flat background in the observed $\mu$SR spectra. This fraction can be ignored in the analysis because $\Delta n$ is determined solely by the relaxation rate. As shown in Fig. 1(c), the implantation depth was scanned from position 1 to 5 by increasing the thickness of the Al degrader. The spatial distribution for each case was calculated with the help of “musrSim” (a Monte Carlo simulation package based on GEANT4) using the known incoming muon momentum along with the

![FIG. 1. (a) Timing diagram of the laser (15 ns FWHM pulse) and muon pulse (70 ns). The laser pulse precedes the muon pulse by the delay t. The muon and laser pulses operate at 50 and 25 Hz, respectively. (b) Schematic diagram of the experimental geometry. Areas in blue (shadowed) illustrate the depth profile of muons distributed in both the Ti window and the sample wafer. (c) Calculated muon stopping distributions (solid blue lines) for five different thicknesses of the Al degrader: 0, 128, 237, 314, and 409 µm for position 1–5 respectively. The histogram bin width is 1 µm. An initial distribution of excess carriers at $t = 0$ is plotted (red broken line) for $\alpha = 16$ cm$^{-1}$. (d) Schematic diagram of the wafer segmented into $N_z$ cells ($d = N_z \Delta z$) along z-axis. A boundary condition is applied to the end cells (filled-in with gray).]
only preparation carried out being solvent cleaning. In this case the wafer was immersed in the warm acetone bath, followed by rinsing with methanol and deionized water; in this process, oil particles and organic residues on the Si surface are loosened and removed. The wafer was then dried with nitrogen gas and loaded into the sample cell under a high-purity He-gas atmosphere. In contrast, Sample B was cleaned with two additional steps to passivate the surface. In this case, after the preparatory solvent clean, the procedure involved a standard RCA clean in an aqueous solution of ammonium hydroxide and hydrogen peroxide, where the hot solution (heated to \( \approx 70 \, ^\circ C \)) removed remaining hydrocarbon residues, oxidized the surface and formed a thin oxide layer. The wafer was then immersed in dilute hydrofluoric (HF) acid (2 %) for approximately three hours. The HF acid etches the silicon dioxide layer and produces a clean H-terminated \(<111>\) surface, whose hydrophobicity can be checked with a wetting test. It is known that this method works particularly well for capping dangling bonds on Si \(<111>\) surfaces by forming covalent Si-H bonds. As a result, wafers prepared in this manner have exceptionary bipolar diffusion.

A 10.5(2) 100(2) — 13.9(2) 0.1326(2)

**TABLE I. Summary of fit results**

| Sample | D [cm/s] | \( \tau_b \) [\( \mu s \)] | S [cm/s] | \( \alpha \) | c [1/cm] |
|--------|---------|-----------------|----------|-----------|---------|
| A      | 10.5(2) | 100(2)          | —        | 13.9(2)   | 0.1326(2) |
| B      | 7.1(3)  | 107(1)          | 106(6)   | 15.9(1)   | 0.1364(4) |

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the fit parameters, $D_i$, $\tau_0$, and $\alpha$, agree with the results from Sample A. This is expected because the wafers are cut from the same single crystal ingot, and these bulk properties should be in the same range. The measured SRV, $106 \pm 6$ cm/s, is significantly slower than the thermal velocity of carriers in Si ($\approx 10^7$ cm/s), but is faster than the reported values for samples immersed in HF acid ($\approx 1$ cm/s). In our setup, it was inevitable that the passivated surfaces on Sample B was exposed to air and slightly deteriorated during the transfer from the HF bath to the purged cell. However, the surface treatment slowed down the SRV sufficiently to allow us to demonstrate the method.

While the fit curves in Fig. 2 generally agree well with the data, small discrepancies can be observed in Fig. 2(a5) and (b5). The reason for this is that the spatial distribution of $\Delta n$ near the surface is highly non-uniform due to the fast SRV. As previously discussed, the method determines $\Delta n$ from the muon spin relaxation rate, which has been averaged over the muon distribution width. If the distribution is centered around the surface, where $\Delta n(z)$ changes significantly over the muon range, the method may not have sufficient spatial resolution to characterize the positional dependence. In addition, the distribution calculation with musrSim assumed exact beam properties, which might be slightly different from the actual beam during the experiment. This will matter most when close to the surface with large values of $d\Delta n/dz$. To resolve these problems, one can simply avoid measuring the surface region, instead increasing the number of depth measurements sampled in the bulk. This should still allow a sufficient number of lifetime spectra to be obtained to allow the parameters determined with good accuracy.

In conclusion, we have demonstrated that photo-$\mu$SR is capable of measuring the CLS at multiple depths in a Si wafer by changing the implantation depth of a muon beam. The depth-dependent lifetime spectra enable us to accurately measure the bulk carrier lifetime and SRV by fitting the spectra to a simple 1-dimensional diffusion model. Unlike other traditional lifetime spectroscopy techniques, the bulk and surface recombination properties can effectively be decoupled using this method, with values independently determined for each. In addition to providing new insights into surface recombination, future work may allow us to determine the intrinsic lifetime limit for Si, which essentially defines the maximum efficiency of Si solar cells. Utilizing the penetrating power of surface muons, the technique can be applied to a complete solar cell to measure carrier lifetimes, thus complementing a measurement that is difficult to make with standard methods. Furthermore, these measurements may benefit from temperature-dependent studies (e.g., to better understand the properties of solar cells used in extreme conditions). These type of measurements would be straightforward with the He-purged sample cell and existing temperature control setup. It is also worth noting that the method should be applicable to other semiconductor systems, as long as the bulk carrier lifetime is sufficiently long (at least a few $\mu$s) so that the $\Delta n(z)$ does not change significantly during the $\mu$SR time window used to determine the relaxation rate. Therefore, we anticipate a wide range of future studies, including active semiconductor materials for power electronics devices, such as silicon carbide, where the carrier lifetime directly relates to the device switching efficiency.

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1. D.A. Neamen, Semiconductor Physics and Devices: Basic Principles, 4th ed. (McGraw-Hill Education, New York, 2011).
2. D.K. Schroder, Semiconductor Material and Device Characterization, 3rd ed. (John Wiley & Sons, Inc., Hoboken, 2006).
3. H. Steinkemper, M. Hermle, and S.W. Glunz, Progress in Photovoltaics: Research and Applications 24, 1319 (2016).
There are a great number of studies on the separation of bulk and surface recombination. Here is a list of only a few representative papers:

1. K.L. Luke and L.-J. Cheng, Journal of Applied Physics 61, 2282 (1987); A. Buczkowski, Z.J. Radzinski, G.A. Rozgoni, and F. Shimura, Journal of Applied Physics 69, 6495 (1991); F.D. Heinz, W. Warta, and M.C. Schubert, Appl. Phys. Lett. 110, 042105 (2017); B. Gaury and P.M. Haney, Journal of Applied Physics 119, 125105 (2016).

2. K. Yokoyama, J.S. Lord, P. Murahari, K. Wang, D.J. Dunstan, S.P. Walker, D.J. McPhail, A.D. Hillier, J. Henson, M.R. Harper, P. Heathcote, and A.J. Drew, Review of Scientific Instruments 87, 125111 (2016).

3. The depolarization mechanism described here is a simplified model. In reality, it involves Mu states in different charge states located at multiple crystalline sites, which form a complex network of dynamic transitions. For further information on the depolarization mechanism in Si, see, for example, Ref. 10 and references therein.

4. K. Yokoyama, J.S. Lord, J. Miao, P. Murahari, and A.J. Drew, Phys. Rev. Lett. 119, 226601 (2017).

5. K. Yokoyama, J.S. Lord, P.W. Mengyan, M.R. Goeks, and R.L. Lichti, Appl. Phys. Lett. 115, 112101 (2019).

6. J.S. Lord, I. McKenzie, P.J. Baker, S.J. Blundell, S.P. Cottrell, S.R. Giblin, J. Good, A.D. Hillier, B.H. Holsman, P.J.C. King, T. Lancaster, R. Mitchell, J.B. Nightingale, M. Owczarkowski, S. Poli, F.L. Pratt, N.J. Rhodes, R. Scheuermann, and Z. Salmon, Review of Scientific Instruments 82, 073904 (2011).

7. K. Yokoyama et al. (2017), STFC ISIS Neutron and Muon Source, https://doi.org/10.5286/ISIS.E.RB1720505