I. INTRODUCTION

Nuclear spins in solid-state systems are compelling candidates for use as qubits. The concept of using donor nuclear spins as qubits in isotopically enriched silicon, originally proposed by Kane, is bolstered by the observations of long coherence times even in integrated single donor devices. In silicon-based donor-quantum dot systems, an electron can be moved on and off the donor using voltages applied to lithographically defined surface electrodes in a lateral quantum dot geometry, creating a heterogenous qubit pair where the electron and nuclear spins interact via the hyperfine interaction. Entanglement between multiple nuclear spins through a simultaneously shared electron has even been demonstrated using this technique. The promise of nuclear spin qubits has been the inspiration for a variety of approaches using donors and isoelectronic spins in silicon.

While much research has focused on electron qubits utilizing quantum dots in silicon, holes in Ge quantum dots have also emerged as promising qubits. Recent advances in the growth of high-quality planar Ge/SiGe heterostructures has led to the rapid development in just a few years of growth of high-quality planar Ge/SiGe heterostructures. Activation of Ga-implanted Ge has been previously characterized for high density ion implantation and a four-hole-qubit device. Hole spin qubits in Ge/SiGe, in contrast to electron spin qubits, have the capability of all-electric control of the hole spin through strong intrinsic spin orbit coupling and exhibit tunable anisotropic g-factors. Together these features open the possibility for simplified and flexible control features in the qubit platform.

The swift and promising emergence of hole-based qubits in Ge/SiGe quantum dots suggests that acceptor-based qubits in germanium also warrant attention. However, in contrast to donors in silicon, acceptor-based qubits have received less attention in the literature. Gallium is one candidate for an acceptor qubit in Ge. It has two stable isotopes at reasonable abundance, $^{69}\text{Ga} (60.11\%)$ and $^{71}\text{Ga} (39.89\%)$; both isotopes have nuclear spin-3/2. The $>1/2$ nuclear spin of the Ga isotopes could allow an individual spin to be controlled through nuclear electric resonance by leveraging the quadrupole moment as was recently demonstrated with $^{125}\text{Sb}$ in silicon. This method avoids the need for oscillating magnetic fields which places constraints on device design. All-electrical control of both the hole spin and nuclear spin in a qubit system would be highly desirable.

An early step to exploring the possibility of using Ga as a nuclear spin qubit is to develop a reliable process for incorporating Ga atoms into substitutional sites of the Ge host crystal at the appropriate densities. Ga atoms can be introduced into a Ge host through growth, thermal diffusion, or ion implantation. Ion implantation is a standard technique for dopant incorporation that allows for great flexibility and is the focus of this work. Following ion implantation, a thermal annealing step is typically required to repair implant damage and activate the implanted Ga atoms by incorporating them into substitutional sites. The activation ratio, defined in this work as the integrated 2D density of charge carriers to the integrated 2D density of implanted Ga atoms, is typically expected to increase with increasing annealing temperature owing to the higher thermal energy available. However, it is also known that at annealing temperatures too high, long range diffusion of dopants may occur, resulting in changes in the dopant distribution profiles and possibly a detrimental loss of dopants through the surface. The goal is to find a tradeoff between dopant activation and dopant loss to achieve the appropriate annealing temperature window.

Activation of Ga-implanted Ge has been previously characterized for high density ion implantation ($>10^{20}$ cm$^{-2}$). Lower fluences ($\leq 10^{12}$ cm$^{-2}$) are commonly used for single dopant spin qubit applications to facilitate individual dopant addressability and minimize interactions between neighbor dopants. Activation of implanted dopants...
strongly depends on the implantation energy and fluence. Thus, these prior studies on dopant activation in the high-fluence regime do not directly translate to the low-fluence regime required for acceptor qubit platforms. Here, we present a systematic study of the activation of implanted Ga acceptors in a Ge substrate as a function of implant density in a low implant fluence regime and rapid thermal anneal (RTA) temperature with the goal of finding appropriate conditions for electrical activation of Ga in Ge.

II. METHODS

We first simulated implanted dopant profiles as a function of implant energy and fluence prior to implantation using the Stopping and Range of Ions in Matter (SRIM) package. Based on the simulated implanted dopant profiles, we chose a beam energy of 175 keV and a maximum fluence of $6 \times 10^{12}$ cm$^{-2}$. This combination spreads the Ga ions over a large enough 3D volume to keep the peak volume density below $10^{18}$ cm$^{-3}$ where dopant clustering may occur which is not desirable for single dopant qubits. Five (100)-oriented commercially acquired Ge wafers of low background doping ($\sim 10^{12}$ cm$^{-3}$) were implanted with Ga ions by Kroko Inc. All implants were performed with a 7° incidence angle to minimize channeling. The Ga fluences for the 5 wafers were $6 \times 10^{10}$, $2 \times 10^{11}$, $6 \times 10^{11}$, $2 \times 10^{12}$, and $6 \times 10^{12}$ cm$^{-2}$, respectively, and were chosen to yield peak Ga densities between $6 \times 10^{15}$ cm$^{-3}$ and $6 \times 10^{17}$ cm$^{-3}$. After implantation the wafers were diced using an automated dicing tool (MicroAuto). Then, the die were annealed in an RTA chamber (Jepelec) for 30 minutes in argon at atmospheric pressure. We explored different anneal temperatures ranging from 200 to 850 °C. This range starts below the minimum temperature required to recrystallize damaged Ge and exceeds the temperature above which the onset of dopant loss is observed.

After the anneal step, selected die were analyzed by spreading resistance profiling (SRP, by Solecon) and secondary ion mass spectrometry (SIMS, by EAG), Raman spectroscopy, and atomic force microscopy (AFM). The SRP characterization determines electrically activated carrier density as a function of depth but does not differentiate between carriers due to activated implanted Ga dopants, preexisting impurities, or damage induced doping. The SIMS characterization evaluates the Ga depth profile but does not differentiate between activated and non-activated Ga atoms. We use these two com-

![Graphs showing SIMS and SRP results](image-url)
FIG. 2. (a) Left y-axis: SRP-derived integrated carrier density. Right y-axis: corresponding activation ratio. The shaded regions divided by dashed vertical lines correspond to anneal temperature ranges exhibiting different effects from Ga dopant behavior: purple denotes unphysical activation ratio suggestive of defects, blue denotes stable electrical activation, and yellow denotes loss of dopants. Inset: SIMS-derived integrated Ga density. All data points shown for fixed implant fluence of $6 \times 10^{12} \text{ cm}^{-2}$. (b) SRP-derived integrated carrier density as a function of implant fluence. (c) Corresponding activation ratio for (b). All data points in (b) and (c) are for samples annealed at 650 °C.

Supplementary techniques to deduce the activation of Ga in Ge. Implant-induced defects in Ge, which are healed by annealing, were qualitatively evaluated as a function of implant and RTA conditions using Raman spectroscopy. Raman spectra were collected using a WITec 300a Raman spectrometer with an excitation wavelength of 532 nm, 18 mW laser power, 600 mm$^{-1}$ grating, 2.0 second integration time, 30 accumulations, and a 100× objective lens. Atomic force microscopy (Digital Instruments Veeco) was used to characterize the surface roughness as a function of the anneal temperature. For the AFM study, an implanted sample with fluence $6 \times 10^{12} \text{ cm}^{-2}$ was thermally annealed six times at incremental increasing temperatures between 600 and 850 °C using the same recipes as the main series of samples. Using a surface defect as a registration mark, we acquired AFM and optical microscope images of the same area on the die prior to the first anneal and in between each of the anneal steps to track surface roughness evolution with annealing.

III. RESULTS AND DISCUSSION

Depth profile distributions of implanted Ga ions were used to evaluate the proportion of activated Ga dopants. Fig. 1(a) shows the SIMS depth profiles of Ga in five different die, each implanted with a Ga fluence of $6 \times 10^{12} \text{ cm}^{-2}$. One die was not annealed (as-implanted) and the remaining four were annealed at temperatures of 550, 650, 750, and 850 °C, respectively. The red squares represent density profiles from a SRIM simulation and agree reasonably well with the as-implanted SIMS density profile between 0 and 180 nm of the surface. As the RTA temperature increases, the SIMS depth profile remains roughly the same until 750 °C at which point a slight broadening of the peak and reduction of the peak height are observable. At 850 °C the distribution becomes flat, indicating significant dopant diffusion and, as seen in the inset to Fig. 1(a), concurrent dopant loss. The increase in the Ga density deeper than ~180 nm for the sample annealed at 850 °C indicates that some dopants are diffusing deeper into the substrate while the inset of Fig. 1(a), which displays the close-up of profiles near the surface, indicates that there is also significant diffusion toward the surface and segregation. Ga dopants appear to accumulate more at the surface as the RTA temperature increases.

Fig. 1(b) shows electrical carrier density profiles derived from SRP. This figure includes data from the same samples as in Fig. 1(a), plus data from a series of samples annealed at lower temperatures. SRP profiles gradually narrow as the anneal temperature increases up to 650 °C, and then rapidly broaden and decrease in amplitude for increasing temperatures above 650 °C. The broadening at high temperatures is consistent with the 750 and 850 °C data shown in Fig. 1(a) for SIMS analysis, suggesting rapid dopant diffusion and loss of dopants at high RTA temperatures.

To further understand the carrier and Ga distribution dependence on the anneal temperature, we plot derived integrated carrier density (left axis) and corresponding activation ratio (right axis) as a function of anneal temperature for samples implanted with fluence $6 \times 10^{12} \text{ cm}^{-2}$ in Fig. 1(a). Here we define activation ratio for each die as the total number of charge carriers derived from SRP measurements divided by the total number of Ga ions derived from SIMS measurements on the particular die annealed at 550 °C. The figure is divided into three shaded regions by anneal temperature: i) $T < 400$ °C (purple), ii) $400 < T < 650$ °C (blue),
and iii) $T > 650 \, ^\circ C$ (yellow). In the first region we observe a large and unphysical (i.e. > 1) activation ratio. Since we defined the activation ratio as the number of free carriers divided by the number of implanted ions, additional carriers must be invoked to explain the unphysical activation ratios > 1 in the purple shaded region of Fig. 2(a).

The unphysical activation ratio and narrowing distributions in Fig. 1(b) at lower anneal temperatures are likely an artifact due to damage induced doping. We used Raman spectroscopy as a probe of implant-induced defects. Raman spectroscopy was carried out on unimplanted, as-implanted, and annealed samples. The implanted samples received a fluence of $6 \times 10^{12} \, \text{cm}^{-2}$, and after $200 \, ^\circ C$, $300 \, ^\circ C$, and $400 \, ^\circ C$ anneal.

The combination of the observed activation ratio, Raman spectroscopy as a probe of implant-induced defects, and the sample’s anneal history suggests that the damage induced doping should be considered in any analysis of Raman data. Figure 3(a) shows normalized Raman spectra of Ge at 200, 300, and $400 \, ^\circ C$. Figure 3(b) shows the TO phonon mode zoomed in vertically to show evolution of low-intensity Ge phonon modes after implant. Figure 3(c) shows the TO phonon mode shift. Data shown here were obtained from a Ge reference, after implanting with a Ga fluence of $6 \times 10^{12} \, \text{cm}^{-2}$, and after $200 \, ^\circ C$, $300 \, ^\circ C$, and $400 \, ^\circ C$ anneal.

FIG. 3. (a) Raman spectra normalized to the 2nd-order TO phonon mode zoomed in vertically to show evolution of low-intensity Ge Raman modes. (b) Normalized TO phonon mode spectra. (c) TO phonon mode shift. Data shown here were obtained from a Ge reference, after implanting with a Ga fluence of $6 \times 10^{12} \, \text{cm}^{-2}$, and after $200 \, ^\circ C$, $300 \, ^\circ C$, and $400 \, ^\circ C$ anneal.
FIG. 4. Dark field images of sample surface following (a) 700 and (b) 750 °C annealing. The red box denotes the AFM scanning area. The large white oval is a surface defect used for image registration (c) RMS roughness acquired with AFM over the area in the red box as a function of anneal temperature. The sample has been implanted with fluence of $6 \times 10^{12}$ cm$^{-2}$.

represented by the blue (center) shaded region of Fig. 2(a). Above 400 °C, the structural defects and strain induced by the implant process itself appears to be removed so that the measured carrier density can be attributed to the Ga ions. Below 650 °C, the surface remains smooth, and surface segregation, Ga diffusion and Ga loss appear negligible. Previous activation studies of Ga-doped Ge at higher densities observed negligible diffusion of dopants for anneal temperatures between 400 °C and 700 °C, consistent with our findings. In this region, activation is reasonable and increases slowly with temperature, which is expected due to the higher temperature enabling more Ga to move onto substitutional sites. The relatively small change in activation ratio versus anneal temperature in this region suggests that the majority of Ga atoms that can move onto substitutional sites have done so.

Having identified an appropriate temperature range for the implant anneal, we turn our attention to the dependence of the activation ratio on implant fluence. Since the activation ratio in this range increases with temperature, we chose the highest temperature within the range (650 °C) to explore the fluence dependence. Fig. 2(c) shows the carrier density profiles derived from SRP for each of the 5 implanted wafers with implant fluences ranging from $6 \times 10^{10}$ to $6 \times 10^{12}$ cm$^{-2}$ for a fixed anneal temperature of 650 °C, and for an unimplanted Ge wafer used as a control. The peak carrier density depth around 50 nm, appears to be independent of the fluence. However, the amplitude of the peak carrier density depends strongly on the fluence and increases faster than the implant density. Fig. 2(b) shows that the SRP-derived integrated carrier density increases superlinearly with the fluence indicating activation improves as the fluence increases. This leads to Fig. 2(c), which shows that the activation ratio increases monotonically from 10% to 64% as the fluence increases from $6 \times 10^{10}$ to $6 \times 10^{12}$ cm$^{-2}$. The monotonic increase in the activation ratio with fluence suggests that a larger fraction of Ga dopants are able to incorporate into substitutional lattice sites with increasing fluence without suffering amorphization effects known to plague implanted germanium at high implant fluences. The highest activation of 64% is comparable to typical measured values from donors implanted in silicon.

In the context of nuclear spin-based qubits, dopants implanted with fluences in the range of those studied in this work yielded successful implementations of individual donor spin qubits in Si, an encouraging figure for future work targeting acceptor spin qubits in Ge.

IV. CONCLUSION

The dopant activation ratios of a series of high purity Ga-implanted Ge wafers were examined as a function of thermal anneal temperature and implant fluence using depth profile measurements and surface analysis studies. We found that the usable annealing temperature range for electrical activation of implanted dopants lies between 400 and 650 °C. At lower temperatures, damage from the implant process appears to result in unwanted excess free carriers, while at higher temperatures dopants are lost via diffusion and surface quality degradation is observed. Additionally, the activation ratio increases with increased implant fluence, and a high degree of electrical activation (near 64%) was obtained at our highest fluence of $6 \times 10^{12}$ cm$^{-2}$. The insights presented here offer a guide towards improving electrical activation of Ga dopants in Ge for eventual studies of all-electric control of acceptor nuclear spin qubits in Ge.

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