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Synthesis and properties of ferromagnetic nanostructures embedded within a high-quality crystalline silicon matrix via ion implantation and nanocavity assisted gettering processes

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Integrating magnetic functionalities with silicon holds the promise of developing, in the most dominant semiconductor, a paradigm-shift information technology based on the manipulation and control of electron spin and charge. Here, we demonstrate an ion implantation approach enabling the synthesis of a ferromagnetic layer within a defect free Si environment by exploiting an additional implant of hydrogen in a region deep below the metal implanted layer. Upon post-implantation annealing, nanocavities created within the H-implanted region act as trapping sites for gettering the implanted metal species, resulting in the formation of metal nanoparticles in a Si region of excellent crystal quality. This is exemplified by the synthesis of magnetic nickel nanoparticles in Si implanted with H⁺ (range: ~ 850 nm; dose: $1.5 \times 10^{16} \text{ cm}^{-2}$) and Ni⁺ (range: ~ 60 nm; dose: $2 \times 10^{15} \text{ cm}^{-2}$). Following annealing, the H implanted regions populated with Ni nanoparticles of size (~ 10 – 25 nm) and density ($\sim 10^{11}/\text{cm}^2$) typical of those achievable via conventional thin film deposition and growth techniques. In particular, a maximum amount of gettered Ni atoms occurs after annealing at 900°C , yielding strong ferromagnetism persisting even at room temperature, as well as fully recovered crystalline Si environments adjacent to these Ni nanoparticles. Furthermore, Ni nanoparticles capsulated within a high-quality crystalline Si layer exhibit a very high magnetic switching energy barrier of ~ 0.86 eV, an increase by about one order of magnitude as compared to their counterparts on a Si surface or in a highly defective Si environment. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4892096>]

I. INTRODUCTION

Research on combining magnetic functionalities with a semiconductor, particularly a Si crystal—the dominant semiconductor in microelectronics, has received a lot attention due to their importance as a possible route to addressing the bottlenecks in the further development of information technologies.¹ In the past few years, many studies have explored the use of ion implantation for implementing magnetic functionalities in Si.^{2–4} In this process, metal ion species (e.g., 3d transition metals) of a desired energy are produced from an ion accelerator and impinged on a Si sample, resulting in a depth distribution of the implanted metal species within the Si. This is a very attractive approach for achieving magnetism in Si since ion implantation has been well established in the semiconductor industry for manufacturing of Si microelectronics devices.

Previous investigations have tended to rely on ion implantation to synthesize magnetic semiconducting Si. Despite the observation of ferromagnetism in metal ion implanted Si, a true magnetic semiconductor in such ion implanted system remains to be identified, and small precipitates formed within the implanted region during ion implantation and post-implantation annealing may be related to the observed magnetism.^{4,5} As suggested by recent experiments

and theories, embedding magnetic nanostructures could offer an alternative to spin injection and collection in semiconductors.^{6,7} For metal ion implanted Si, the local environments immediately surrounding the magnetic regions contain an unacceptable level of defects created by heavy ion implantation,^{2–4} rendering such system inapplicable for spintronics devices, since the presence of a large density of structural defects inhibits the generation of spin polarized electrons in Si.

Our current work presents a different approach to form magnetic nanoparticles in Si regions of a high crystal quality, based on two phenomena related to interactions between implanted ions and crystal defects in Si: (1) the production of nanometer-sized cavities by H⁺ ion implantation at a location beyond the metal ion implanted region as a result of the degassing of molecular hydrogen resulting from the accumulation of implanted H atoms at vacancies,⁸ and (2) the trapping/gettering of metal atoms at the nanocavity sites well below the metal ion implanted range due to the presence of a high density of unsaturated dangling bonds on their inner walls.^{9–12} Since the crystal damage in the H-implanted region can be readily recovered following annealing, the adjacent surroundings of metal nanoparticles resulting from these processes would possess an excellent crystal quality, unlike the case in the metal ion implanted region.

Metal gettering at nanocavities created by H⁺ ion implantation has been shown in previous work, but the magnetic properties of the resultant metal nanoparticles have

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never been studied and it is not clear whether such phenomena could be capitalized on for synthesis of magnetic nanostructures embedded in a Si matrix of a high crystal quality. In our current work, a detailed analysis of the structural and magnetic properties of Si coimplanted with Ni^+ and H^+ ions indicates that the Ni nanostructures formed in an optimal annealing condition could exhibit ferromagnetism even at room temperature, and they are immediately surrounded by a Si environment with few defects following a full recovery of crystal structures in the H-implanted region. The resultant high-quality crystalline Si regions with embedded ferromagnetic nanostructures would serve as a base material structure for implementing viable spintronic devices, e.g., devices could be constructed with the highly defective layer (the initial metal-implanted region) near the surface etched off to allow spin-polarized electron flowing within the regions of a high crystal quality.

Our work also helps address a peculiar issue related to the applications of magnetic nanoparticles. As the size of magnetic particles approaches the nanometer scale, they would evolve into the so-called super-paramagnetic state, which leads to complete loss of net magnetization due to the random flipping of moments of particles at a temperature above the blocking temperature¹³ (typically much lower than the Curie temperature). This problem may be alleviated by forming magnetic nanoparticles in a crystalline matrix, which may lead to an increase in the magnetic anisotropy of nanoparticles if the interactions between nanoparticles and their surroundings are properly engineered.^{14,15} In this context, Si is also an attractive material as the hosting matrix for magnetic nanoparticles due to its dominance in the semiconductor industry as well as its high thermal and structural stability.

II. EXPERIMENT

Samples were prepared by sequentially implanting a n-type Si (100) wafer with H ions at 100 keV (projected range ~ 850 nm) to a dose of $1.5 \times 10^{16} \text{ cm}^{-2}$ as well as Ni ions at 70 keV (projected range ~ 60 nm) to a dose of $2 \times 10^{15} \text{ cm}^{-2}$ using a Varian Extron 400 implanter. The energies/ranges of implanted Ni^+ and H^+ ions were selected to ensure a large spatial separation between two implanted regions. This will confine the highly damaged Ni-implanted region close to the surface, which can be readily etched off during device fabrication, and in the meantime will minimize the impact of crystal damage created by Ni ion implantation on the generation of nanocavities in the H-implanted region. The Ni^+ implant was done with the sample temperature at 300°C so as to minimize the implantation induced crystal damage in the near-surface region. Following implantation, the samples were annealed between 700 and 1000°C in ultra-pure argon ambient for 60 min. This caused the implanted H^+ ions to escape the Si sample, leaving spherical nanocavities at depths close to the H^+ ion projected range. In the meantime, the implanted Ni atoms diffused away from the surface region and some of them were trapped in the nanocavities. Si control samples were prepared in the same way except without the step of H ion implantation.

Rutherford backscattering spectroscopy/channeling (RBS/C) measurements were performed using a 2 MeV

helium ion beam produced from a Dynamitron accelerator, to evaluate the crystal quality in ion implanted Si, as well as the occupation of Ni atoms in the Si lattice. Due to the difficulty of RBS in detection of the Ni atoms that may be located deep below the surface (~ 850 nm), secondary ion mass spectroscopy (SIMS) was conducted using an IONTOF TOF.SIMS 5 with a time of flight (TOF) detection scheme to determine the redistributions of implanted Ni caused by the annealing processes. High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL 2010F electron microscope with 200 keV electrons to acquire the information of the resultant nanostructures in Si samples. In addition, energy filtered TEM imaging for Ni elemental mapping was performed using electrons with energy loss ~ 855.5 eV (L_{III} edge of Ni) in an energy window ~ 30 eV. The magnetic properties of the samples were characterized using a Quantum Design MPMS-XL superconducting quantum interface device (SQUID) magnetometer and confirmed by a Quantum Design VersaLab vibrating sample magnetometer (VSM) for selected samples.

III. RESULTS AND DISCUSSION

A. Crystal damage and recovery

Fig. 1 shows the RBS/C spectra of the Si samples implanted with H^+ and Ni^+ ions and annealed at different

FIG. 1. RBS/Channeling spectra for the as-implanted and annealed samples: (a) with both H and Ni implants, and (b) with only Ni implant. Insets show the blow-up of the Ni signals.

temperatures. A disruption to the crystal structure is indicated by a rapid increase in the scattering yield of channeled He^+ ions by Si atoms. In addition to a peak (channel number 570–580) related to ion scattering from Si surface atoms, the scattering peaks for the Si signals, one around channel number 325–380 (~ 850 nm in depth) and the other around channel 540 (~ 30 nm in depth), arise from crystal damage created by H^+ and Ni^+ implantations, respectively. The Si crystal recovers following post-implantation annealing, as suggested by the diminished intensities of the damage peaks.

For both the samples with and without the H^+ ion implant, following Ni^+ ion implantation at 300°C , the RBS yield for Ni atoms in the implanted region decreases by $\sim 70\%$ when the analyzing ion beam was aligned in the $\langle 100 \rangle$ direction (Fig. 1). This implies that most implanted Ni atoms may occupy a lattice location shadowed by Si atoms in the $\langle 100 \rangle$ direction. As reported before,¹⁶ one possibility for such lattice location is the tetrahedral interstitial site in the Si unit cell. The remaining 30% of the implanted Ni atoms, appearing at random locations in the lattice, is likely in the form of nickel silicide precipitates,^{17,18} as evidenced in our TEM measurements.

As mentioned above, one major drawback related to the approach of directly forming metal nanoparticles in the metal ion implanted Si region is that the resultant nanoparticles are immediately surrounded by a local environment having a large amount of crystal defects induced by such heavy ion implantation. Our current work intends to form Ni nanoparticles in the H-implanted layer rather than the heavily damaged Ni-implanted region. To assess the defect retention, we compare the ion scattering intensity from the implanted region with that from a defect-free reference at the same depth. For the H-implanted region, the scattering yield from the defect-free reference has been corrected for ion dechanneling effects caused by the Ni implanted region near the surface. Fig. 2(a) shows the ratio of the RBS yield for the H-implanted region relative to that expected for the defect-free reference at the same location. The ratio has the maximum of ~ 2.5 following implantation, and decreases with annealing. In particular, the ratio reaches ~ 1.0 , implying that the 900°C anneal has fully recovered the Si lattice structure in the H-implanted region.

This is not the case for the Ni-implanted region in the same sample showing a high density of defects. Even after

annealing at 900°C , the ion scattering intensity from the Ni-implanted layer remains a factor of ~ 1.8 with respect to the defect-free reference (e.g., a virgin Si sample) at this depth, indicating the presence of disordered Si atoms at a high density $\sim 2.6 \times 10^{20}/\text{cm}^3$. The situation is much worse in the sample implanted with Ni only. There the defect density in the Ni-implanted region increases by $\sim 40\%$ compared to the sample with dual implants. In previous investigations² on ion implantation in Si for magnetism, the ion dose of implanted metal species is typically higher than that in our experiment, and thus those Si samples are characterized by a defect density much higher than $2.6 \times 10^{20}/\text{cm}^3$, even after high-temperature annealing.

The excellent recovery of crystal quality in the H-implanted region is also confirmed on the microscopic scale. The TEM micrograph (Fig. 2(b)) shows two distinct layers of structures within the Si implanted with both Ni^+ and H^+ ions after annealing at 900°C . The first layer extending from the surface to the depth of ~ 150 nm, corresponds to the Ni implanted region, and the other of a thickness 100 nm, located ~ 750 nm below the surface, results from the H^+ ion implantation. The contrast in brightness between these two layers indicates a difference in their defect retention. Specifically, even after annealing at 900°C , the Ni-implanted region remains very defective. Selected area electron diffraction from the H-implanted layer (Fig. 2(c)) yields a clear diffraction pattern related to the $\langle 110 \rangle$ zone axis of the Si lattice, indicating an excellent crystal quality in the H-implanted layer after annealing, consistent with the RBS/C results. In addition, TEM shows the presence of nanocavities in the H-implanted region after annealing.

Interestingly, the addition of H^+ ion implantation seemed to alleviate the damage accumulation in the Ni implanted region. For example, RBS/C data show that after annealing at 700°C , the ion scattering yield for the sample with only Ni^+ implant is about twice the scattering yield for the sample with both Ni^+ and H^+ implants. In addition, a reverse annealing effect occurred for the sample implanted with Ni only, where the ion scattering from the Ni implanted layer after annealing at 700 and 800°C became even stronger than the as-implanted situation. We attribute such reverse annealing phenomenon to the effects of nickel silicide mediated crystallization of the amorphous Si zones within the Ni implanted region. The nickel silicide precipitates formed

FIG. 2. Scattering intensity vs annealing temperature for the H and Ni implanted regions after annealing (b) TEM image showing the distinct surface and cavity band region for the 900°C annealed sample (c) High resolution TEM micrograph showing the needle-like nickel silicide precipitates in the Ni implanted region (d) Selected area $\langle 110 \rangle$ electron diffraction pattern from the nanocavity band showing clear diffraction spots.

during annealing can act as heterogeneous nucleation sites for displaced Si atoms to recrystallize; and as the silicide precipitates migrate, a trail of Si crystallites of needle-like morphology forms within the matrix,¹⁹ which is also confirmed by our HRTEM morphology (Fig. 2(d)). Since these Si nano-crystallites grow on the NiSi₂ (111) planes, with their crystal orientations much different from the Si substrate, a much higher rate of dechanneling would be expected as the aligned ions reach these “grain boundaries” between such nano-crystallites and the Si matrix. In the case with both H⁺ and Ni⁺ implants, the reverse annealing effect only occurs at 800 °C, to a much smaller degree. This is because H induced nanocavities serve as sinks for Si interstitials to decrease their accumulation in the implanted region,²⁰ favoring the formation of single-crystal structures in the Ni implanted region by suppressing nucleation of displaced Si atoms at silicide precipitates.

B. Formation of Ni nanoparticles via gettering

As shown by SIMS measurements (Fig. 3), substantial redistribution of implanted Ni occurs following annealing. The as-implanted sample exhibits a Ni concentration profile extending to a depth ~ 400 nm, much deep beyond the Ni ion range of ~ 60 nm, which is expected to result from the occurrence of Ni atomic diffusion during the hot implantation process with the substrate temperature at 300 °C. For the Si samples implanted with Ni only, a substantial amount of the implanted Ni diffuses away from the near-surface region upon annealing, e.g., only $\sim 1\%$ of the total implanted Ni atoms being detected after the 900 °C anneal. This is quite different from the case for the Si samples implanted with both Ni⁺ and H⁺. There, the areal density of Ni in the top 500 nm Si region (on top of the H-implanted layer) increases significantly after annealing at high temperatures (>800 °C). For example, the Ni atom density in the top 500 nm layer reaches $\sim 4.4 \times 10^{14} \text{ cm}^{-2}$ at 900 °C, more than a factor of ~ 4.6 compared to the case at 800 °C. Annealing of the Si implanted with both H⁺ and Ni⁺ also results in the relocation of Ni from the implanted region to the H implanted region (600–800 nm). After annealing at 900 °C, $\sim 1.0 \times 10^{15} \text{ cm}^{-2}$ of Ni or almost 50% of the total implanted dose has been relocated to the H-implanted region. The trapping of implanted Ni atoms in the H-implanted region is a

consequence of diffusion assisted transport of Ni atoms followed by their subsequent chemisorption on the walls of nanocavities created in the H implanted region.²¹

As the implanted samples are annealed, two competing processes take place: the diffusion of Ni out of the implanted region, and the Ni silicide formation in the near surface region. At low temperatures (<700 °C), the dominant silicide formed in Ni-implanted Si is believed to be the NiSi phase, and a transformation to the NiSi₂ phase occurs at higher temperatures.²² For the Si implanted with Ni only, the Ni atom density decreases with annealing temperatures, implying that the diffusion process is much faster than the silicide formation in such sample. The Si implanted with Ni⁺ and H⁺ exhibits a different trend: the near-surface Ni density decreases after annealing up to 800 °C, but the 900 °C anneal causes it to even exceed the level in the lower temperature cases. We attribute this different behavior to the effects of H induced nanocavities on the formation of nickel silicide.²³

Once Ni atoms getter at nanocavities or structural defects, their diffusion rate drops below that for the trap-free diffusion case, due to a reduction in the concentration gradient. Such trap-limited diffusion process may help retain Ni atoms in the near surface region to form silicide. For low temperature annealing, the gettering effects on the overall redistribution of implanted Ni atoms are rather weak, and thus the near-surface Ni atom densities of two types of samples are similar to each other. Instead, a much greater amount of Ni atoms are found to trap at nanocavities after annealing at 900 °C, which leads to retarded diffusion of Ni atoms and thus a significantly enhanced generation rate for silicide (NiSi₂) phase formation in the near-surface region for the sample implanted with both H⁺ and Ni⁺ implants.

The formation of Ni nanoparticles as a result of gettering of implanted Ni at H induced nanocavities is revealed by transmission electron microscopy (Fig. 4). Energy-filtered Transmission Electron Microscopy imaging shows strong evidence for the existence of Ni nanoparticles around the end of H⁺ ion projected range. Nanoscale structures containing Ni atoms are also found in the Ni implanted near-surface region, which are likely related to Ni silicide precipitates since they exhibit much weaker magnetism compared to Ni nanoparticles formed in the nanocavity layer, as seen in Sec. III C. From HRTEM analysis, the average size of the cavities is found to increase with the annealing temperature, from

FIG. 3. TOF-SIMS depth profiles showing (a) the Ni redistribution to nanocavity band on annealing for samples with both H+Ni implants, and (b) areal densities of Ni at the Ni implanted and the H implanted regions after annealing at different temperatures.

FIG. 4. (a) Energy-filtered TEM micrograph corresponding to Fig. 2(b) showing the Ni-enriched regions (brighter spots) in the Ni and H implanted regions; (b) The average areal density and diameter of nanocavities after annealing at different temperatures. High resolution TEM micrographs showing the cavity walls decorated or partially filled with Ni for (c) 700 °C, (d) 800 °C, and (e) 900 °C annealed samples, respectively.

~15 nm at 700 °C, ~20 nm at 800 °C to ~25 nm at 900 °C. With the information of the cavity size and density (Fig. 4(b)) and assuming a spherical cavity shape, one may estimate the total areal density of Ni atoms that would completely fill up the volume of the created nanocavities. As an example, in order to completely fill up the void corresponding to a cavity areal density of $\sim 7.3 \times 10^{10} \text{ cm}^{-2}$ produced by annealing at 900 °C, it would require a Ni density at the level $\sim 5 \times 10^{16} \text{ cm}^{-2}$, which is one order of magnitude more than the density of Ni atoms relocated in the H implanted layer as detected by SIMS. This vast difference indicates that only a small fraction of nanocavities are being filled up with Ni atoms, as seen in HRTEM images (Figs. 4(c)–4(e)) showing that the Ni only decorated the cavity walls for 700 and 800 °C annealed samples whereas more volume of the cavities is filled for the sample annealed at 900 °C. It should be noted that our approach has led to the formation of embedded Ni nanoparticles with size and density comparable to those typically achievable via more conventional thin film deposition/growth techniques.

C. Magnetic properties of Ni nanoparticles embedded in Si

Fig. 5 shows the magnetization (M) vs. magnetic field (H) curves for the Si samples. During the magnetization measurement, a maximum external magnetic field of 1600 Oe with increments of 100 Oe was applied parallel to the sample surface and the diamagnetic background of the Si matrix was removed. The as-implanted samples before annealing show no signs of magnetism. After annealing, the Si sample implanted with Ni^+ only exhibits a narrow hysteresis loop with a coercivity value less than 50 Oe, almost independent of annealing temperatures. The magnetization curves are typical of ferromagnetically blocked single-domain features, and a mix of ferromagnetic and superparamagnetic behaviors for

magnetic particles of various sizes is not the case, since potbellied or wasp-waisted loop shapes were not seen.^{4,24}

The origin of such observed magnetism in the Si implanted with Ni^+ only is not clear. According to first-principle calculations considering the effects of crystal field splitting, p-d coupling and exchange interactions on the level filling of Ni 3d⁸ electrons, the magnetic moments of Ni

FIG. 5. Magnetic moment vs applied field for samples annealed at different temperatures: (a) implanted with Ni only and (b) implanted with both H + Ni.

atoms occupying either the substitutional or interstitial locations in Si crystal would be zero.²⁵ Although none of the commonly observed nickel silicides is known to be magnetic,²⁶ one may not completely rule out the existence of a weak itinerant ferromagnetic nickel silicide or small clusters, similar to the manganese doped Si.^{4,6} If this were the case, such nanomagnets of Ni precipitates should have a blocking temperature less than 10 K.²⁷

For the sample with dual implants, the measured hysteresis loops vary strongly with annealing temperatures. After annealing at 700 °C, the magnetization curve exhibits little opening even at 3 K. As the annealing temperature increases to 800 °C, the magnetization loop starts to open up with a coercivity value of ~ 100 Oe and a non-zero remanence, but no saturation in magnetization was observed even at the highest applied field. The M vs. H plot for the 900 °C sample, on the other hand, shows a wide hysteresis loop with a large coercive field ~ 300 Oe, characteristic of a ferromagnetic-like behavior. On the other hand, the magnetization saturation for the 700 °C annealed sample seems to be lower than the 800 °C annealed sample, but the 900 °C anneal results in the lowest amount of saturated magnetic moments.

The comparison in magnetization behaviors and microstructures between two types of Si samples implies that ferromagnetism observed for these samples is of different origins. For annealing at 700 and 800 °C, these Si samples exhibit much stronger magnetism, even though their respective Ni density in the near-surface region is lower than that in the Si implanted with Ni⁺ only. It is worth mentioning the case of annealing the sample with dual implants at a temperature as high as 1000 °C, where the near-surface density of Ni atoms reaches a maximum ($\sim 10^{15}/\text{cm}^2$) but no Ni atoms are detected in the nanocavity region due to the collapse of nanocavities at such extreme temperature. The magnetization curve of the 1000 °C annealed sample exhibits insignificant coercivity *albeit* a large saturation moment, similar to the samples implanted with Ni only. These results indicate that Ni nanoparticles formed within H induced nanocavities via gettering play a key role in the strong ferromagnetism as demonstrated in Si with both H and Ni implants.

As seen from the structural analysis, the 700 °C anneal yields a relatively large density ($2.6 \times 10^{11}/\text{cm}^2$) of nanocavities but a small number ($1.1 \times 10^{13}/\text{cm}^2$) of Ni atoms trapped at these cavities. Consequently, both the size and the number of resultant Ni nanoparticles are small, and each of them would be isolated from the other with a large interparticle distance, thus leading to low coercivity and low magnetization saturation. As the annealing temperature increased to 800 °C, the nanocavity density decreases to ($1.1 \times 10^{11}/\text{cm}^2$) and the amount of Ni being trapped at the nanocavities increases by a factor of ~ 40 compared to the 700 °C anneal. This implies an increase in the number of Ni nanoparticles in the nanocavity layer, thus leading to a high saturation magnetization. For annealing at 900 °C, a diminished density ($7.3 \times 10^{10}/\text{cm}^2$) of nanocavities and an increase in nanocavity size due to Ostwald ripening, compounded with a high density ($1.0 \times 10^{15}/\text{cm}^2$) of Ni atoms gettering at nanocavities, result in the formation of a smaller number of relatively large (~ 25 nm) Ni nanoparticles,

as suggested by a very low level of saturation in magnetization.

D. Implications on magnetic anisotropy and particle interactions

More details can be extracted regarding the magnetic properties of Ni nanoparticles formed in the dual-implant Si during annealing at 900 °C. If all the gettered Ni atoms are uniformly dispersed among all created nanocavities to form nanoparticles, there would be 10^4 Ni atoms in each nanoparticle of diameter ~ 3 nm. At such particle size, Ni nanoparticles would not exhibit the observed ferromagnetic-like characteristics, as indicated by the magnetic measurements on the Si sample implanted with Ni only. In fact, not every nanocavity has been filled up by gettered Ni atoms, as shown in the TEM images (Fig. 4). This is because metal atoms are preferentially filling the relatively small cavities due to their high surface energy density.²⁰ So one may arrive at a lower bound of magnetic moment as $\sim 2970 \mu_B$ per Ni nanoparticle, or as $\sim 0.22 \mu_B$ per Ni atom, after dividing the saturated magnetization by the number of nanocavities or the number of gettered Ni atoms, respectively. For comparison, the magnetic moment per atom in the Ni bulk crystals $\sim 0.61 \mu_B$. The magnetic moment per atom for Ni nanoparticles is expected to decrease from the value close to the isolated atom case toward the corresponding bulk value as the nanoparticle size increases.²⁸ This low magnetic moment may result from an overestimate of the number of Ni atoms contributing to magnetism, since a large fraction of Ni atoms trapped at nanocavities could be in the form of non-magnetic silicide.¹⁰

For comparison, we also estimate the magnetic moment for smaller nanoparticles formed at a lower annealing temperature (e.g., 800 °C). Since the magnetization of such sample did not reach saturation at the highest field applied during our experiments, we extract the saturated magnetization by performing a Langevin fit to the M vs. H data. The result yields the saturation magnetic moment of 4.2×10^{-6} emu for the 800 °C annealed sample, leading to $\sim 8300 \mu_B$ per 20 nm Ni nanoparticle or $\sim 2 \mu_B$ per Ni atom within the nanoparticle, after dividing the total sample moment by the number of nanoparticles or trapped Ni atoms, respectively. As expected, both magnetic moment values of the smaller (20 nm) nanoparticles are greater than their counterparts of the larger (25 nm) nanoparticles. For the 800 °C annealed sample, the magnetism arising from small Ni precipitates in the Ni-implanted layer may not be ignored compared to that derived from those Ni nanoparticles in the H-implanted layer. We thus divide the saturated magnetization by the total amount of Ni atoms in both the near-surface and nanocavity regions, yielding a magnetic moment of $\sim 1.4 \mu_B$ per Ni atom. This is much smaller than the magnetic moment value ($5 \mu_B$) expected for a single isolated Ni atom, but remains too large compared to previously reported values for Ni nanoparticles of a similar size.²⁸ The discrepancy may result from an overestimate of the saturation magnetization by using the Langevin function. This issue is not expected to occur for the 900 °C annealing case, where the magnetization should be dominated by the contribution of Ni nanoparticles in the nanocavity layer, and the effect of those

Ni atoms in the surface region on magnetism is negligible because the Ni precipitates in the near surface region have much smaller size compared to the Ni nanoparticles in the deep layer, and additionally, most of the Ni atoms in the near-surface region may exist predominantly in the form of silicide rather than small Ni precipitates as a consequence of a much higher rate for silicide formation during high temperature annealing.

As shown in Fig. 6, the coercivity value gradually decreases with the measurement temperature. The data are fitted to the following relation describing the temperature dependence of coercivity $H_C(T)$ for an ensemble of randomly oriented non-interacting particles: $H_C(T) = H_M \left[1 - \left(\frac{T}{T_B} \right)^{1/2} \right]$, where H_M corresponds to the coercivity at 0 K, and T_B is the blocking temperature.²⁹ According to the Stoner-Wohlfarth model, if a remnant to saturation moment ratio, M_r/M_s , is greater than 0.5, Ni nanoparticles are interacting with each other. In our case, the M_r/M_s ratio is ~ 0.68 at 3 K but decreases quickly with measurement temperatures, implying the above equation could be used as a reasonable approximation to describe our samples. The fitting result yields a T_B value of ~ 400 K, which indicates an energy barrier for magnetic switching as $25 k_B T_B$ or ~ 0.86 eV, being almost one order of magnitude of that found for Ni nanoparticles of similar or larger size deposited on a Si surface.³⁰ This high blocking temperature is also supported by the observation of magnetic hysteresis loops even at room temperature (inset in Fig. 6).

Compared to the case with Ni nanoparticles on the Si surface, our result suggests that encapsulation of Ni nanoparticle within a Si matrix with excellent crystal quality has led to a dramatic increase in magnetic switching energy. The hysteresis loops in our samples are symmetric in both the positive and negative directions of the applied in-plane field, showing no sign of the exchange bias effect, which should rule out the possibility of increased magnetic anisotropy due to ferromagnetic-antiferromagnetic interactions of the Ni nanoparticle cores with their surrounding (e.g., an oxidized shell).^{13,31} Possible contributions to the magnetic switching energy include magnetocrystalline anisotropy, shape

anisotropy, and surface/interface anisotropy. The formed Ni nanoparticles are in the spherical-like shape, and their shape anisotropy is expected to be negligible.¹³ The magnetic anisotropy constant for 25-nm Ni nanoparticles in our Si sample is estimated to be at least on the order of $\sim 1.6 \times 10^4$ J/m³, about three times the anisotropy constant in bulk Ni material,³² implying that the interface between Ni particles and their Si surroundings may play a key role in magnetic switching of embedded Ni particles.³³ Alternatively, magnetoelastic anisotropy due to strains around magnetic nanoparticles may not be ignored.^{34,35}

In addition to enhanced surface/interface anisotropy, the inter-particle interactions may be partially responsible for the persistence of hysteretic behavior for Ni nanoparticles at room temperature. One of the possible inter-particle interactions is the dipolar interaction between Ni nanoparticles.¹³ With an approximation to the dipolar interaction energy, $E_{d-d} = n(\mu_0/4\pi k_B)(m^2/D^3)$, and assuming the nearest neighbor number of 12, we can estimate the strength of dipolar interactions in the 900 °C annealed sample containing 25-nm Ni nanoparticles with inter-particle distance of $D \sim 50$ nm as determined by TEM analysis and of magnetic moment $m \sim 3000 \mu_B$ as measured from the magnetization characterization. The interaction strength is on the order of 4×10^{-5} eV, indicating that the dipolar interaction does not contribute to the increased magnetic barrier as observed in our work. Another type of inter-particle interactions could be the exchange interaction, but the Ni nanoparticles (filled nanocavities) are separated by ~ 50 nm, well exceeding the magnetic exchange length (~ 20 nm) in Ni.³⁰ Whether an indirect exchange process assisted by carriers in Si occurs in this system would be an interesting issue for investigations in the future.

IV. SUMMARY

To summarize, we have demonstrated the formation of Ni nanoparticles embedded in a Si matrix of excellent crystal quality, through gettering Ni atoms from their initially implanted region to nanocavities created by H⁺ ion implantation in a deeper region. As the amount of gettered Ni atoms in the nanocavity layer increases with annealing temperature, the magnetic properties of the Si are dominated by these Ni nanoparticles formed via the nanocavity assisted gettering process. In particular, a maximum atom density of gettered Ni occurs following annealing at 900 °C, resulting in strong ferromagnetism persisting even at room temperature. Compared to Ni nanoparticles on a Si surface, the resultant Ni nanoparticles embedded in a Si crystal can have a much higher switching energy barrier, likely arising from a significantly enhanced surface anisotropy. Our scheme for synthesis of magnetic nanoparticles embedded in Si is based on ion implantation—a well-established technology for Si integrated circuits, and different from previous work using ion implantation to create magnetism within a heavily damaged region, our scheme can lead to the formation of ferromagnetic nanoparticles in a selected crystalline Si region of a high crystal quality, therefore opening up new opportunities for achieving viable spintronic devices in Si.

FIG. 6. Coercivity vs temperature plot with the theoretical fit. Inset shows the magnetization curve for the 900 °C annealed sample measured at 300 K.

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