Synthesis of magnetic nanoparticles by low-energy dual ion implantation of iron and nickel into silicon dioxide followed by electron beam annealing

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Abstract: Magnetic nanoparticles have been made by low-energy dual ion implantation of iron and nickel into SiO₂ with a nickel fluence ratio of 82% followed by electron beam annealing for 1800 s at 1000°C. After annealing, there is significant diffusion of iron and nickel into the silicon dioxide layer. Annealing also led to the formation of superparamagnetic nanoparticles with a narrow particle size distribution. The saturation moment at 5 K was 0.7 µB.
and a similar value was observed at 300 K, which indicates that the Curie temperature is far above room temperature. This moment is lower than that expected for Ni_{0.82}Fe_{0.18}. While the results clearly show the formation of superparamagnetic nanoparticles, it is not possible to determine whether nickel–iron, iron or nickel has formed.

**Keywords:** ion implantation; nanoparticles; superparamagnetism; permalloy; magnetisation; Rutherford backscattering.


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## 1 Introduction

Magnetic nanoparticles can potentially be used in a wide variety of applications including magnetic sensors [1], high-density data storage [2], magnetic contrast agents [3] and other magneto-electric devices [4]. The various conventional methods to synthesise nanoparticles include chemical synthesis [5], polyol synthesis [6], laser ablation [7], and arc discharge [8]. Ion implantation is a novel method that could potentially be used to synthesise magnetic nanoparticles with unique properties tailored to suit different applications [9–11]. Near-surface iron nanoparticles have previously been synthesised in SiO₂ films using low-energy ion implantation followed by electron beam annealing [9,10]. They have a number of properties that are not observed for the bulk compounds. For example, it is possible to obtain nanoparticles that exhibit superparamagnetism at room temperature if the nanoparticle size is small enough. Superparamagnetism occurs when the thermal energy is greater than the magnetocrystalline anisotropy energy [12]. This property is of interest because it can lead to magnetic sensors with negligible hysteresis allowing magnetic fields to be measured to low fields even after exposure to
high magnetic fields [13]. It is also possible that the nanoparticles have a large magnetoresistance, which is useful for device applications [10]. Current ion implantation studies have focussed on magnetic materials that have a relatively large magnetocrystalline anisotropy energy and hence a relatively small superparamagnetic radii at room temperature [9–11,13,14]. It would be interesting to explore other magnetic nanoparticles made by ion implantation that have a low magnetocrystalline anisotropy energy. This could possibly be achieved by making nickel–iron superparamagnetic nanoparticles, where the magnetocrystalline anisotropy energy can be as low as 0.4% of that observed in iron [12]. The resulting superparamagnetic radii limit can be as high as 50 nm at room temperature.

In this paper, we report the results from a Rutherford backscattering and magnetic study of films containing iron and nickel that were made by low-energy dual ion implantation followed by electron beam annealing. Electron-beam annealing was selected because it has previously been shown that this method leads to magnetic nanoparticles after ion implantation [9]. We show below that the dual iron and nickel implantation and electron beam annealing leads to superparamagnetic nanoparticles.

2 Material and methods

Iron and nickel ions were implanted into 500 nm thick silicon dioxide films on silicon substrates that were 0.275 mm thick. This was followed by electron-beam annealing at 1000°C in a high vacuum. The implantation was performed with the low-energy metal implanter at GNS Science, Lower Hutt, New Zealand [9,10,15]. The implantation of \(^{58}\text{Ni}^+\) was done at room temperature at normal incidence with an energy of 10 keV and a current of <2 µA. The fluence was 2 × 10\(^{16}\) at./cm\(^2\) and the pressure was 10\(^{−7}\) mbar. \(^{56}\text{Fe}^+\) was implanted into the nickel-implanted samples under identical conditions with a fluence of 4.5 × 10\(^{15}\) at./cm\(^2\). The nickel to iron fluence ratio was 82%. Electron beam annealing [15] was done by ramping to a 1000°C at a rate of +5°C/s, holding at 1000°C for 1800 s and then cooling to room temperature at a rate of −0.8°C/s. Simulations using Dynamic TRansport of Ions into Matter (D-TRIM) software package were used to estimate the nickel and iron implantation depth and concentration profile. Rutherford backscattered spectrometry (RBS) measurements were performed using a 2 MeV He\(^+\) beam and current of ~20 nA. Magnetisation measurements were performed on a Quantum Design SQUID magnetometer.

3 Results and discussion

The results from D-TRIM simulations of the nickel and iron concentration profiles are shown in Figure 1. The simulated theoretical peak depth of nickel in the silicon dioxide film is 15 nm and the maximum depth is 35 nm. These theoretical depths are similar for iron implanted after the nickel implantation. The distribution profile indicates that 18 at.% of the particles at the peak concentration are nickel. At these nickel concentrations, there is a balance between sputtering and implantation leading to a less Gaussian-like distribution and a higher concentration near the surface [9].

The data from RBS measurements are shown in Figure 2 after e-beam annealing at 1000°C for 1800 s. The Fe/Ni peaks are indicated in the figure as well as the Si at the
SiO₂/air interface, the Si at the Si/SiO₂ interface, and the oxygen in the SiO₂ layer. It is not possible to distinguish between iron and nickel owing to the limits of the energy resolution of the surface barrier detector of the RBS, which is around 20 keV, and because the sample is not isotopically pure. The calculated fluence was $1.05 \times 10^{16}$ at.cm$^{-2}$. It can be seen that the Fe/Ni peak is broad and asymmetric at lower energies, which indicates that there is considerable diffusion into the SiO₂ film. This is indicative of migration of the ions and a change in thickness of the implanted region. Iron and nickel undergo Fickian diffusion through the oxygen vacancies in silicon dioxide [16,17]. Previous measurements on iron implanted into SiO₂ and electron-beam annealed for 3600 s at the same temperature of 1000°C also showed diffusion of the implanted ions into the film as well as the formation of iron nanoparticles that protruded from the surface [9,10]. The fluence of the iron in that case was $1 \times 10^{16}$ at.cm$^{-2}$, the energy used was 15 keV, and the mean implantation range was 12 nm [9]. The diffusion rate of nickel in silicon dioxide is higher than that of iron [16,17] and this possibly leads to nickel further into the film and an iron-rich surface in our film.

Figure 1  D-TRIM simulations showing concentration profiles after implantation of Ni into SiO₂ with an energy of 10 keV and Fe into Ni-implanted SiO₂ showing a maximum depth of 35 nm and a peak depth of 15 nm (see online version for colours)

The results from magnetic measurements as a function of the applied magnetic field at 5 K and 300 K can be seen in Figure 3. Here the data are plotted as the moment per implanted ion, $m_{\text{Ni,Fe}}$, that was obtained from the measured moment $m$, using $m_{\text{Ni,Fe}} = m/(n \times A \times \mu_B)$, where $n$ is the fluence, $A$ is the area and $\mu_B$ is the Bohr magneton. It can be seen in Figure 3 that the sample is ferromagnetically ordered and the moment saturates above ~0.2 T. The saturation moment per implanted ion, $m_s$, at 5 K is 0.70 ± 0.12 $\mu_B$ and it is similar at 300 K, where it is 0.62 ± 0.08 $\mu_B$. This indicates that the Curie temperature is significantly above room temperature. $m_s$ at 5 K is lower than that expected for nickel–iron alloy (0.95 $\mu_B$) with a Ni concentration close to 82% [18]. If the implanted ions have formed nickel–iron nanoparticles then the measured $m_s$ would correspond to ~74% of the material being nickel–iron and the remaining material could be antiferromagnetic iron and nickel oxides. $m_s$ at 5 K is comparable to that of nickel (0.6 $\mu_B$) and hence it is also possible that there are nickel nanoparticles after electron beam annealing. However, this would require the segregation of iron and nickel and the
formation of antiferromagnetic iron oxides or isolated paramagnetic iron atoms. There are further possibilities that even include the formation of ferromagnetic Fe$_3$O$_4$ that has a saturation moment of 4 $\mu_B$ [19] as well as the formation of antiferromagnetic nickel oxides. However, iron oxides have not been observed in previous studies of iron implantation followed by electron beam annealing and hence this scenario would appear to be unlikely.

**Figure 2** Rutherford backscattering data from nickel–iron films after annealing at a 1000°C for 1800 s

![Rutherford backscattering data](image)

**Figure 3** Plot of the moment per implanted ion against the applied magnetic field at 5 K (red circles) and 300 K (black circles) for the nickel–iron implanted film after electron beam annealing at 1000°C for 1800 s (see online version for colours)

![Plot of moment](image)

The results from the zero-field-cooled (ZFC) and field-cooled (FC) temperature-dependent magnetisation measurements at 10 mT are shown in Figure 4. There is a peak in the ZFC data at 150 K and absence of hysteresis above 280 K. This is indicative of superparamagnetic nanoparticles, where there is a distribution in the nanoparticle
Synthesis of magnetic nanoparticles by low-energy dual ion

size [9]. Superparamagnetism occurs when the thermal energy is greater than the magnetocrystalline anisotropy energy [12]. It is possible to estimate the nanoparticle radius, \( r \), from the blocking temperature using the equation \( r = \left( \frac{75 k_B T_B}{4 \pi K_{\text{eff}}} \right)^{1/3} \), where \( T_B \) is the blocking temperature (150 K), \( K_{\text{eff}} \) is the effective magnetocrystalline anisotropy energy, and \( k_B \) is the Boltzmann constant. Using the magnetocrystalline anisotropy energy of nickel–iron alloy, 200 J m\(^{-3}\) [12], in this equation, the average radius of the nanoparticles from the blocking temperature of 150 K is calculated to be ~40 nm. The appearance of hysteresis up to 280 K indicates that there are some nanoparticles that are larger than this that have a maximum blocking temperature of 280 K and the resultant nanoparticle radius is 45 nm. This would indicate a relatively narrow nanoparticle size distribution. Using the magnetocrystalline anisotropy energy for iron (4.8 \times 10^4 J m\(^{-3}\) [12]), the calculated average particle size is ~6.4 nm, and it is ~14 nm for Ni using the nickel magnetocrystalline anisotropy energy (~0.5 \times 10^4 J m\(^{-3}\) [12]). On the basis of the current magnetic data, it is not possible to definitively say whether nickel–iron nanoparticles or other magnetic nanoparticles have formed, although it is clear from the data that superparamagnetic nanoparticles have formed. For this reason, we are planning a more detailed transmission electron microscopy and magnetisation study with different annealing conditions.

Figure 4 Plot of the zero-field-cooled and field-cooled magnetisation against temperature in a magnetic field of 10 mT for the nickel–iron implanted film that was electron beam annealed at 1000°C for 1800 s (see online version for colours)

4 Conclusions

In conclusion, we have implanted nickel and iron into silicon dioxide using a low energy dual ion implantation method with the Ni fluence ratio being 82% and this was followed by electron beam annealing at 1000°C for 1800 s. RBS results after electron beam annealing showed that there is diffusion of the implanted ions further into the film. Magnetic measurements showed that electron beam annealing leads to the formation of superparamagnetic nanoparticles. The saturation moment per implanted ion at 5 K is 0.70 ± 0.12 \( \mu_B \). This is less than that expected for nickel–iron alloy with a similar concentration (0.95 \( \mu_B \)). If nickel–iron nanoparticles are formed, then the saturation
moment per ion would correspond to ~74% of nickel–iron with the remainder being antiferromagnetic iron and nickel oxides. However, the moment is comparable to that of nickel and hence it is also possible that there are superparamagnetic nickel nanoparticles as well as antiferromagnetic iron oxides. There are also a range of other possibilities. On the basis of the blocking temperature ($T_B = 150$ K) obtained from the ZFC-FC magnetisation data, the radius of the nanoparticles would be ~40 nm if a nickel–iron alloy was formed and ~6.4 nm or ~14 nm for iron or nickel nanoparticles, respectively. There is hysteresis in the ZFC-FC curves up to 280 K, which indicates that there is a narrow range in nanoparticle sizes. It is not possible with the current data to determine if the superparamagnetic nanoparticles are nickel–iron, iron or nickel. Further measurements are currently being performed with different annealing durations to better understand the magnetic phases that occur after e-beam annealing.

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References

Synthesis of magnetic nanoparticles by low-energy dual ion


