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Fabrication of Gd Nanoparticles in SiO₂/Si Substrate by Ion Implantation

J.Kennedy^{1*}, J. Leveneur¹, P.P. Murmu¹, P. Anilkumar², A. Iqbal²,

¹National Isotope Centre, GNS Science, PO Box 31312,
Lower Hutt, New Zealand.

²Department of Physics and Nanotechnology, SRM University,
Chennai, India

*Corres.author: j.kennedy@gns.cri.nz

Abstract: Magnetic nanoclusters and nanoparticles find vast application in spintronic devices, magnetic random access memory, and magnetic sensors. Gadolinium (Gd) nanoparticles were fabricated by low energy (23.5keV) Gd implantation into SiO₂ followed by vacuum thermal annealing at 1000°C. Transport of ion in matter simulations (using Dynamic TRIM) shows that the maximum depth of implantation is 25nm and the implanted ion concentrations centered at 15 nm. Rutherford backscattering spectrometry was used to measure the implanted Gd concentration in as-implanted and annealed samples. The ion beam analysis results are complemented by topography measurements using atomic force microscopy. We report a preliminary investigation of growth of Gd nanoparticles on the surface of SiO₂. Low implantation fluence $\leq 10^{16}$ at. cm⁻² leads to pinholes and no significant surface nanoparticles formation. Nanoparticles were observed only after large implantation fluences $\geq 2 \times 10^{16}$ at. cm⁻². This nanostructure fabrication method has potential in nanoscale sensors fabrication.

Keywords: Implantation; nanoparticles; Dynamic TRIM; Rutherford backscattering spectrometry; Atomic force microscopy.

Introduction

Materials composed of discrete isolated nanoparticles with size dependent electronic properties, have a wide range of potential applications. The oxide dielectric matrices containing dispersed metal nanoparticles are promising materials for applications in optoelectronics and magnetic sensors [1]. Several physical and chemical methods have been used to produce nanoparticles on a substrate. These include: ion implantation, sol and sol-gel, sputtering, pulsed laser deposition, cluster beam deposition and flame synthesis [2-4].

Ion implantation is a precise technique and is compatible with existing microelectronics fabrication methods. Ion implantation has been used extensively to fabricate a wide variety of nanostructured materials. A common feature of nanoparticles is that the surface dominates their properties due to the large surface to volume ratio. Embedded nanoparticles or nanoclusters can be very durable since they are protected from the surrounding environment, which can be a critical issue depending on the nanoparticles reactivity. The near-surface region that is formed by ion beam synthesis has properties that can have important technical advantages

over conventional thin films and homogeneous bulk nanophase materials. Ion implantation and conventional oven annealing have been used in previous studies to synthesise nanoclusters and nanoparticles in semiconductors.

Magnetic nanoparticles have also been synthesised using ion implantation and they showed interesting properties and they can potentially be used for spintronics applications.[5] The implantation step is often followed by an annealing step that leads to atomic reorganisation, healing of defects, and further growth of the nanoparticles.[4]. Understanding the ion implantation and annealing process is crucial to ensure reproducible material properties. In the previous reports, our group has demonstrated formation of transition metal magnetic ion nanoparticles fabrication and electrical, structural and magnetic properties. Here we report the first series of results on fabrication of Gd nanoparticles at the surface of SiO₂-Si.

Experimental

To synthesise Gd nanostructures, Gd⁺ ions were implanted with fluences ranging from 5×10^{15} to 10^{16} at. cm⁻² at 23.5 keV under normal incidence into 300 nm thermally grown amorphous silicon oxide on silicon wafer substrate using GNS Science low energy ion implantation facility [6]. The ion beam was raster scanned over the surface to produce a laterally homogeneous implantation into the films. The implanted samples were then cut in half and subsequently annealed using vacuum furnace annealing system. The samples were annealed for 1 hour at 600-1000°C at high vacuum (2×10^{-7} mbar).

Rutherford Backscattering Spectrometry (RBS) is a well-known technique to evaluate the composition of materials surface down to the nanoscale [7]. RBS measurements were undergone using the 3 MV Van-de-Graaff accelerator at GNS Science. Spectra were collected using a 2.0 MeV ⁴He⁺ beam and a current of 20-30 nA. The samples were mounted on a computer controlled stepping motor and a collimated (1.5 mm slit type) surface barrier detector was set at a scattering angle of 165°. The solid angle of the RBS experimental arrangement was 0.075 msr.

Results and Discussion

Dynamic TRIM [8] simulations for various doses between 5×10^{15} and 5×10^{16} at. cm⁻² are shown in Figure 1 (left). The simulations revealed a mean projected range of 15 nm coupled with a maximum implantation depth of around 25 nm. For these fluences, the Gd peak concentration varies between 5 and 17 at.%. At a fluence larger than 1×10^{16} at. cm⁻², the Gd profile intersects with the surface. For fluences larger than 2×10^{16} at. cm⁻² the concentration on the surface is more than 2 at.%. Hence, for larger fluences it is likely that precipitation occurs close to the surface.

A typical RBS spectrum obtained for an as-implanted sample is shown in Figure 1 (right). RBS peaks associated with Gd can be seen to appear at channel number 640, whereas the Si and O backscattering peaks appear at around channel numbers 320 and 250, respectively. In the as-implanted samples, it can be seen that Gd intensity increase systematically according to the implantation fluences.

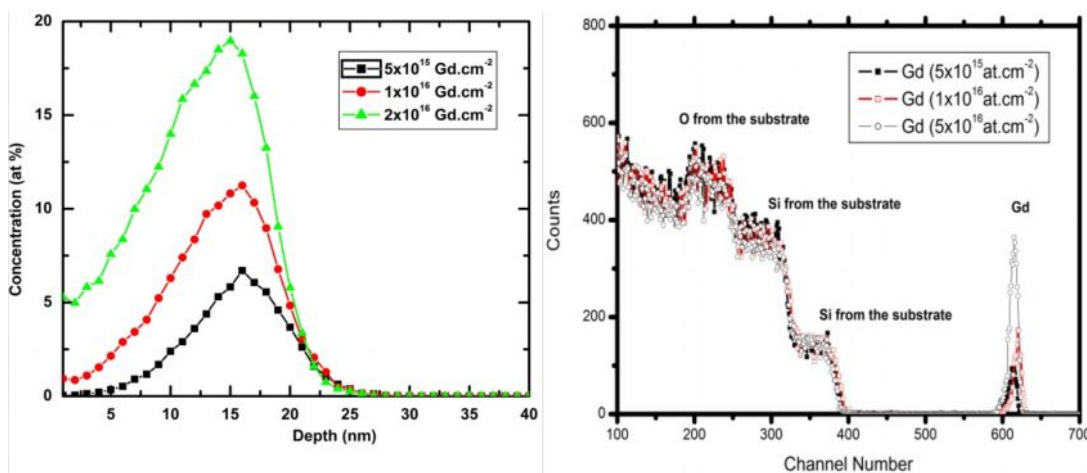


Figure 1 (Left) Gd depth profiles simulated with Dynamic Trim, (Right) RBS spectra of Gd implanted silica.

Atomic Force Microscope (AFM) measurements were carried out on the as-implanted and vacuum annealed samples to obtain information on their topography. As implanted samples did not show any significant structures on the surface. During annealing low fluences samples showed formation of pinholes and small 1-2 nm nanostructures on the surface. The average depth of the observed pinholes was 24 ± 4 nm with the deepest hole observed at about 50 nm. The depth is coherent with the penetration range of the Gd ions presented above. Pinhole formation is known to occur during high temperature vacuum annealing of SiO_2 and arises from the desorption of SiO_2 in SiO gas molecules[9] but was not observed in Fe implanted samples[4]. As shown on Figure 2 (left), even after 4 hrs the surface shows similar features. However, the surface of the samples implanted with the larger fluences $\geq 2 \times 10^{16} \text{ cm}^{-2}$ appear not to develop the pinholes and present nanoparticles formation of about 10-30 nm.

In conclusion, the potential for fabrication of gadolinium nanoparticles on an amorphous SiO_2 substrate with low energy ion implantation was investigated. Ion beam analysis techniques proved to be very useful for the quantitative determination of the composition of ion implanted materials. Different surface features were observed with varying fluence and annealing conditions. The annealing process induces pinholes formation, with depth close to the expected implantation range, and the coalescence of precipitates. While the formation of nanoparticles on the surface for large implantation fluences is to be expected due to larger Gd concentration, the observed enhanced pinhole formation needs further investigation. The structure and composition of the observed nanostructures will also undergo further characterization.

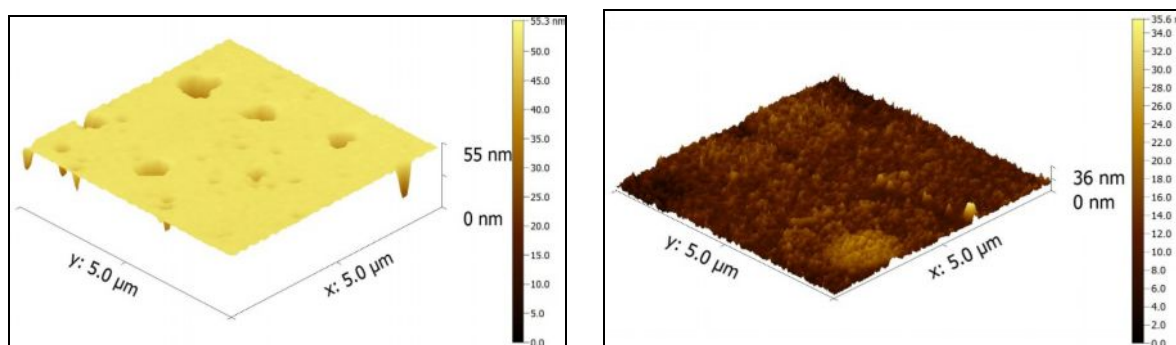


Figure 2. AFM image of 23 keV Gd implanted with (left) a fluence of 10^{16} cm^{-2} followed by vacuum annealing at $1000 \text{ }^\circ\text{C}$ for 4 hour and (right) a fluence of $5 \times 10^{16} \text{ cm}^{-2}$ followed by vacuum annealing at $1000 \text{ }^\circ\text{C}$ for 1 hour.

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