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Ion Implantation Study of Rare-Earth Doped Strontium Titanate

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Abstract : Ion implantation is a suitable technique to alter the near surface properties of a material. In particular, it can be used to synthesize magnetic nanogranular surfaces. In this preliminary study, the effect of Gadolinium (Gd) ion implantation at various fluences in bulk strontium titanate ($SrTiO_3$)was investigated. Implantation was carried out at the energy of 30keV. Dynamic-TRIM simulations were performed to predict the depth profiles of the implanted ions and concentration.Implantations were subsequently followed by a high vacuum furnace annealing at 650°C.Rutherford backscattering spectrometry (RBS)was undertaken to evaluate the changes in Gd concentration in $SrTiO_3$. AFM was used to evaluate the topography of the samples before and after annealing. SQUID measurement was carried out to determine the presence of a potential magnetic response resulting from the modification induced by ion implantation and annealing. Magnetization results showed magnetic ordering at low temperature withmoment up to ~3 $\mu_B$perGd ion. The technique shows promising results which encourage for further investigation into near surface modification of $SrTiO_3$for spintronics and sensor applications.

Introduction

There is a considerable interest in developing new nanogranular ferromagnetic/insulator materials and new synthesis methods to produce such materials. Indeed, the transport, magnetic and magneto-optical properties in this class of materials have shown promising results which could be applied in a range of application varying from novel spin based electronics to magnetic sensors, magnetoelectric and data storage applications[1,2,3,4].We have demonstrated previously the formation of ferromagnetic and superparamagnetic nanoparticles in SiO_2 on Si which displayed large room temperature magnetoresistance that has potential for use in large magnetic field sensors[5].

Strontium titanate ($SrTiO_3$)is a material with a cubic perovskite structure with large dielectric constant. As a single crystalline substrate it has been used for the hetereoepitaxial growth of novel materials showing interesting properties such as ferromagnetic ordering[6],ferroelectricity[7], high temperature superconductivity[8], and colossal magneto resistance[9].Previously, various ion implantation into $SrTiO_3$ has been investigated to produce different nanogranular layers which includes gold[10], cobalt, and manganese[11], and iron[12].Gadolinium (Gd) shows room temperature ferromagnetic ordering andis a potential candidate for the synthesis of a ferromagnetic nanoprecipitate.

In this paper, we investigate the formation of a Gd precipitate by low energy ion implantation into $SrTiO_3$ and annealing induced diffusion and changes in topography. We also present early evidence towards the onset of magnetic ordering after Gdimplantation and annealing that has potential in synthesizing ferromagnetic nanoprecipitates in dielectric materials.

Experimental

The ion implantation process was carried out at 30 keV for fluencesrangingfrom1 $\times10^{15}$ to 5×10^{16} Gd cm^{-2} into $SrTiO_3$substrate using low-energy ion implanter at GNS Science[13]. The vacuum inside the implantation chamber was maintained at around 2×10^{-7}mbar throughout the implantation process. Ion transport in matter simulationswere carried out using Dynamic TRIM to predict the depth profiles of Gd into $SrTiO_3$[14]. A set of samples was subsequently annealed in a high vacuum furnace (base pressure ~ 7×10^{-7} mbar)using a quartz tube at 650 °C for 1 h.

The samples were characterized by Rutherford backscattering spectrometry (RBS),particle-induced X-ray emission (PIXE)to retrieve their structural and compositional analysis. RBS consists in measuring the energy of recoiled incident atoms at a given geometry to retrieve the depth profile and elemental composition in the materials. PIXE makes use of X-rays produced from electronic transition arising from the excitation of electrons under the ion bombardment. The X-ray lines are characteristics of the elements encountered which enable unique identification ofthe composition of the material. These experiments were undertaken using a 2 MeV He^+ beam with a beam current of 15 nA, and the recoiled particles were detected using a surface barrier detector placed at 165°[15].Atomic force microscopy (AFM) was used to analyse the topography of the films using a NanosurfEasyscan 2 software package. The magnetic response at 5 K was investigated usinga magnetic property measurement system and the data were obtained from a superconducting quantum interference device (SQUID) magnetometer from Quantum Design.

Results and Discussion

Transport of ion in matter simulations

Dynamic TRIM (D-TRIM) simulations were performed at 30 keV for fluences of1 $\times10^{15}$,$5\times10^{15}$and 1 $\times10^{16}$Gd cm^{-2}into $SrTiO_3$. The obtained results from the D-TRIM simulations are shown in Fig. 1. The Fig. 1 shows that Gd atoms are located at an average depth of ~12.6 nm from the surface. It can be observed from the simulated plots that the concentration of Gd increased from approximately 1 at.% to 9 at.% with increasing the fluences. The distribution profiles intersect the surface rapidly with increasing the fluences leading to Gdconcentrations of about 2.5 at. % and 7.5 at.%for 5×10^{15} and 1 $\times10^{16}$Gd cm^{-2}, respectively, at the surface. Simulations also indicate that a significant portion of bombarded Gd atoms are getting recoiled and sputtered out of the samples. This leads to a lower fluencethan the theoretical values after implantation.

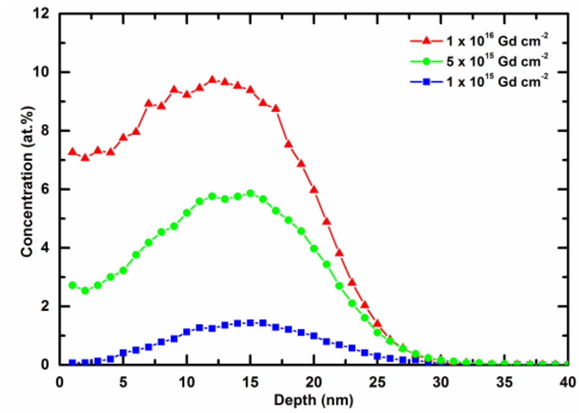

Fig. 1: Dynamic TRIM Simulation for 30 keVGd into $SrTiO_3$.

Ion beam analysis

RBS technique was utilized to retrieve the composition of the Gd implanted $SrTiO_3$and monitor potential diffusion during the annealing process. RBS results showed the presence of Gd in the implanted samples and are located in the near-surface layer consistent with the D-TRIM calculations. The actual implanted concentrations (retained doses) were retrieved from the RBS spectra using the RUMP software package. For1 $\times10^{16}$Gdcm^{-2} samples the retained dose was 7.5×10^{15}Gd cm^{-2}. This differs from the nominal fluence because of the preferential sputtering of Gd atoms which is a common trait for a low-energy and high fluence implantation[16].

Figure 2 shows the comparative Gd peaks obtained from RBS spectra of as-implanted and annealed samples. A decrease in the Gd concentration is observed after annealing without significant broadening of the peak. This loss can be attributed to the diffusion or loss of Gd due to the vacuum annealing at 650°C.PIXE spectra confirmed the elemental composition observed with RBS and hinted no contamination within the technique's detection limit.

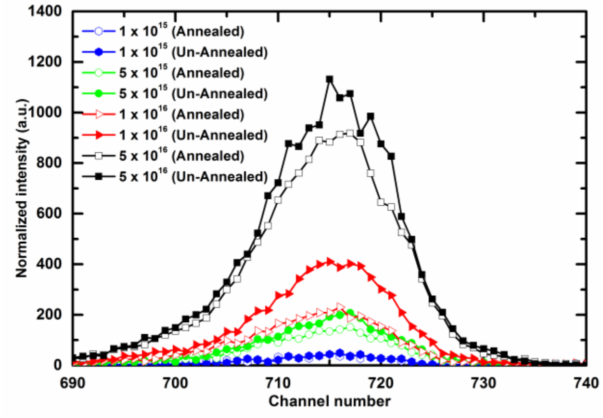

Fig. 2: Gd peaks extracted from the RBS spectra for un-annealed (full) and annealed samples (empty).

Magnetic response

A preliminary SQUID magnetization measurement was taken for the 1×10^{16}Gd cm^{-2}sample at 5 Kacross the applied magnetic fields of ±6 T. $SrTiO_3$ is diamagnetic even at low temperature[17].The observed magnetic response clearly shows onset for different magnetic ordering above the diamagnetic contribution (linear component of the curve) from $SrTiO_3$ as seen in Fig. 3. The magnetic moment was found to be $3\pm0.4\mu_B$ per Gdion, where diamagnetic response was subtracted out and the data is normalized against the concentration retrieved from RBS. This is consistent with the presence of a Gd rich ferromagnetic and/or paramagnetic precipitate. In fact, if all the Gd ions are considered to be present in high spin state then they will contribute 7 μ_B per Gdion. Moreover, Gd metal have been observed to couple ferromagnetically with a moment up to 7.63 μ_B per Gd atom[18].Gdnanoprecipitate were also reported with effective moments ofabout1.05μ_B per Gd atom in Gd implanted ZnO[19].These results are encouraging and invite further investigation of the nature and origin of the observed magnetic ordering at room temperature which should include temperature dependence of the magnetic moment.

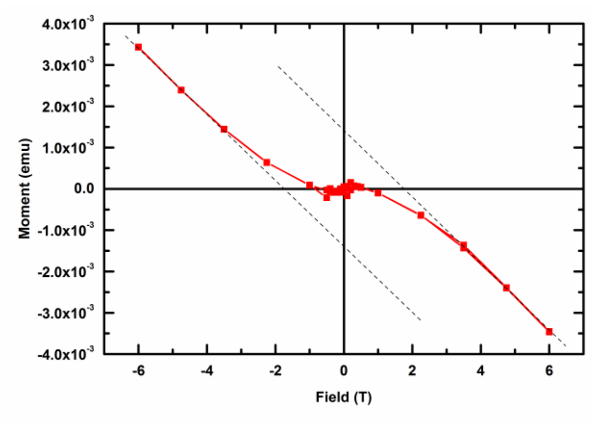

Fig.3:Magnetic momentofa1 $\times10^{16}$ Gd cm^{-2}into $SrTiO_3$at 5 K against the applied magnetic field. The dashed lines highlight the diamagnetic component of the magnetic response.

Surface structure

The AFM images of the as-implanted samples did not show significant changes on their surface morphology with various implantation conditions. However, a change was observed on their surface morphology after annealing. This is unexpected as the Gd concentration profiles are seen to intersect the surface as observed in D-TRIM calculations. It could be due to the fact that the initial roughness of the materials could be masking small changes occurring in the surface topography upon annealing the samples. The surface topography of the 1 $\times 10^{16}$ Gd cm^{-2}implanted and 650 ^{o}C annealed samples didn't show any further significant change over the initial roughness.

Conclusions

In conclusion, we present the preliminary results obtained from compositional and magnetic measurements on Gd implanted into $SrTiO_3$. Ion beam analysis results showed that Gd atoms are incorporated into the $SrTiO_3$ matrix at the near surface region. At higher fluences, retained dose was slightly lower than the implanted fluence which is due to the preferential sputtering a common trait observed in a low-energy and high fluence ion implantation. AFM images did not show any significant changes on their morphological properties upon annealing. However, magnetization data revealed magnetic ordering at low temperature with moment up to ~3 μ_B per Gd ion. Our results suggest that rare-earth doping into dielectric substrates such as $SrTiO_3$ has the potential for fabrication of magnetic nanogranular particles for spintronics and sensor applications.

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