Electronic structure and magnetic properties of Ni phases embedded in CeO₂ thin films

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INTRODUCTION
In the field of nano-science/nanotechnology, the energetic ions are of use for both synthesis and modification of the nanomaterials [1-5]. The important issues in the nanomaterial synthesis are (i) tailoring the shape of nanostuctures, (ii) control of the size of particles, and (iii) size distribution. Ion beams play a significant role related to all these issues [1-2]. There are two ways of nanostructuring by ion beams, namely: swift heavy ion (SHI) irradiation and ion implantation. In SHI irradiation (ion having energy of a few 100 MeV to a few GeV) the ions lose their energy by electronic energy transfer rather than nuclear energy loss process [1-2]. As a consequence of high energy deposition within a very short span of time, track of molten zone is formed along the ions trajectory. This molten zone solidifies within picoseconds. As a result of the rapid quenching of the material, nanocrystallization may take place within the matrix [6] and even near the surface of the sample [7-8]. In the ion implantation process, the energetic ions have low energy (a few tens of keV to a few hundreds of keV). The desired ions can be implanted in the suitable matrix by choosing the various implantation parameters, like: type of ion, ion energy, range of ion, and ion fluence etc. The implanted ions get embedded in the host matrix and form crystalline phases of nano-sized regime. There are several reports available on the synthesis of embedded metallic nanophasess by ion implantation technique followed by annealing, in insulating matrix [9-11].

Recently, the synthesis of embedded magnetic nanostructures in insulating/di-electric matrix has gained much interest as these systems are promising for the application in nonlinear optics, high density magnetic storage devices, and magnetic sensors [12-13]. F. C. Fonseca et al. [14] has performed a detailed characterization on Ni nanoparticles embedded in a SiO₂ amorphous matrix using sol-gel technique. They found that above Tₘ=40 K the Ni nanophases embedded in SiO₂ matrix exhibit superparamagnetic. They observed that the metallic Ni particles were free from an oxide layer and evidenced by the absence of exchange bias in hysteresis loops taken at temperatures below Tₘ. A.L Stepanov et al. [15] used ion implantation for modifying the physical and chemical properties of TiO₂ matrix. They synthesized solid solutions by implanting the Fe ions and demonstrated the anisotropic ferromagnetism at room temperature. From above reports, it is inferred that the ion implantation technique offers spatial selectivity and depth control of the doped species and, hence, stands far ahead over the other doping methods, like chemical synthesis and solid state reaction methods. Further, a common characteristic of embedded nanostructured magnetic materials is the coexistence of two or more phases, magnetically and/or structurally different, which are modulated on a length scale of the order of a nanometer. Therefore, these systems offer challenges in their synthesis and understanding of physics behind them. There are several issues to be answered before realization of these systems for practical applications, like: (i) identification of different metallic/oxide nanophases, (ii) understanding of lattice – host exchange interaction, and (iii) spin-dependent coupling mechanisms. X-ray diffraction (XRD) has been widely utilized to determine phase/structure and detect the presence of small sized secondary phases. X-ray absorption (XAS) technique using synchrotron radiation has proven its capability not only for phase determination but also for the investigation of local structure of the target material. The XAS measurements provide information about the charge state, local environment, and hybridization of specific cations present in the material [9-10]. Such techniques may also help in the understanding of the electronic interaction among the dissimilar atoms in case of embedded/doped systems. In this...
context, we employed (the elemental specific) XAS measurements at different elements edges to understand the role of embedded Ni nanophases on the structural and magnetic properties of CeO₂ thin films.

**EXPERIMENTAL**

CeO₂ thin films were grown by the pulsed laser deposition (PLD) method at a deposition temperature of 400 °C and an oxygen partial pressure (PO₂) of 10⁻⁴ Torr. A circular target of 1 inch diameter was prepared from the commercial CeO₂ powders (Sigma-Aldrich, 99.9% purity) and the films were deposited on quartz substrate. The substrate was cleaned with tri-chloro-ethylene, acetone and methanol using an ultrasonic cleaner prior to deposition. The KrF excimer laser of wavelength 248 nm with repetition rate of 10 Hz and energy density of 1.8 J cm⁻² was used to ablate the target material. The target-substrate distance was kept 4 cm. After deposition, the films were cooled down slowly to room temperature (RT) under the same PO₂ as used during deposition. After deposition, the film thickness was determined by a profilometer. Thus estimated film thickness was ~200 nm. Implantation of 80 keV Ni⁺ ions (current density of 1.5 μA cm⁻²) was performed into CeO₂ thin films at RT in a vacuum chamber of 1.3×10⁻⁷ Torr using source of negative ions by Cesium sputtering at Inter University Accelerator Centre (IUAC), New Delhi, India. The implantation fluences were selected according to the Ni percentage in CeO₂ matrix (i.e., x = Ni/Ce+Ni). Then the implanted samples were post annealed in air at 600 °C for 4 hours to recover the structural damage caused by implantation. According to Monte-Carlo ion-range simulation code SRIM2006, the projected range and straggling of Ni ions of 80 keV are ~38 nm and ~1 nm, respectively, in CeO₂. The formation of the Ni nanostructures was investigated by x-ray diffraction using Bruker D8 advanced diffractometer with Cu Kα radiation (λ = 1.540 Å). The electronic structure of the samples has been investigated by XAS measurements. Near edge X-ray absorption fine structure (NEXAFS) spectra at the Ni L-edge were collected in the total electron yield (TEY) mode at 10D (PAL-KIST) beam line. Ce L-edge X-ray absorption near edge spectroscopy (XANES) spectra were collected in TEY mode at 1D beam line of PAL under the stationary conditions. 1D beam line is a bending magnet X-ray scattering (XRS) beam line and uses a Si(111) double crystal monochromator to provide a wide range of energies (4 - 15 KeV). Higher harmonics were effectively removed by detuning of crystals to 70% of the peak width of the empty 3d-valence states, while the oxide spectra exhibit considerable fine structure, called multiplet structure. Multiplet interaction of the 3d electrons with neighboring atoms [16]. The two main peaks in the L₂,₃-edge spectra of 3d metal elements arise from the spin orbit interaction of the 2p core shell and the total intensity of the peaks is primarily proportional to the number of empty 3d valence states. The metal spectra mainly show two broad peaks, reflecting the width of the empty d-bands, while the oxide spectra exhibit considerable fine structure, called multiplet structure. Multiplet effects arise from the spin and orbital momentum coupling of different 3d valence holes (or electrons) in the electronic ground state, and from coupled states formed after x-ray absorption between the 3d valence holes and e g-holes. 

**RESULTS AND DISCUSSION**

Figure 1 shows the XRD patterns (plotted in log scale) of as-deposited and Ni implanted CeO₂ thin films. The amount of Ni implantation in CeO₂: films are mentioned in each panel of figure. It is clear from the figure that the as-deposited film shows three diffraction peaks of (111), (311) and (222) planes of fluorite - type CeO₂ (space group Fm-3m) with face-centered-cubic unit cell of CeO₂ (JCPDS#780694). This further validates the deposition of (111) textured CeO₂ thin films on the amorphous quartz substrate. Implantation with low Ni concentration (2 at.%) does not show any measurable changes in the XRD patterns of the films, within the detection limit of used x-ray diffractometer. Further increase in the Ni concentrations leads to formation of nickel oxide phases, an indicative of the solubility limit of Ni in CeO₂ by implantation technique. At the highest Ni concentration (7 at.%) a few peaks of Ni metal are detected with the Ni oxide phases. This is an indication of the formation of metallic Ni and Ni oxide nanophases in the CeO₂ matrix. Very low intensity of the observed Ni peaks makes it difficult to calculate the grain size of so formed nano-phases. From the diffraction profile analysis of the Ni (222) peak, an average grain size of Ni nanostructures (for 7 at.% Ni doped CeO₂) was calculated to be ~6 nm by using Scherrer relation (D = 0.9λ/β Cosθ).

**Figure 1.** (color online) XRD patterns of as-deposited and Ni implanted CeO₂ thin films.

The NEXAFS measurements involve the excitation of electrons from core level to the partially filled and empty states. The peak position and spectral features of the NEXAFS spectra are affected not only by the oxidation state of probed ion, but also by its structural symmetry and covalent/ionic character of the bonds between cations and neighboring atoms [16]. The two main peaks in the L₂,₃-edge spectra of 3d metal elements arise from the spin orbit interaction of the 2p core shell and the total intensity of the peaks is primarily proportional to the number of empty 3d valence states. The metal spectra mainly show two broad peaks, reflecting the width of the empty d-bands, while the oxide spectra exhibit considerable fine structure, called multiplet structure. Multiplet effects arise from the spin and orbital momentum coupling of different 3d valence holes (or electrons) in the electronic ground state, and from coupled states formed after x-ray absorption between the 3d valence holes and e g-holes.
and L_{2} (2p_{3/2} to 3d transition) edges of Ni atom. It can be seen from the figure that the spectral features of all Ni implanted CeO_{2} thin films partially matches with the spectral features of NiO (indicated by B and C) and Ni metal (indicated by A). For clarifying our assumption, we de-convoluted the Ni L_{2,3} edge of all the Ni implanted CeO_{2} thin films and presented in the Figure 2 (b). It is clear from the Fig. 2 (b) that area under the peak A (which is the signature of Ni metal peak) increased with increasing the concentration of Ni in the samples. Thus, the Ni L_{2,3} – edge spectra of Ni implanted CeO_{2} thin films indicate the formation of mixed phases of Ni metal and Ni oxides in CeO_{2} matrix.

To further analyze the effect of Ni doping on the valence state of Ce ions, systematic, XANES spectra at Ce L – edge have been collected and presented in the Figure 3. The assignment of the transitions in the spectra is made based on the earlier reports [18-19]. The component D is assigned to core excited Ce^{4+} final state with the configuration 2p_{4/2}5d_{1}, where 2p_{4/2} denotes a hole in 2p shell (with J = 3/2), while 5d{1} refers to the excited electron in the 5d state. The peak C is also a Ce^{4+} peak with final state 2p_{4/2}4f_{1}5d_{1}L_{6}, which denotes that in addition to an electron excited from Ce 2p shell to 5d shell, an-other electron is also excited from the valance band (O 2p shell) to Ce 4f shell, leaving a hole in the valence band (presented by L_{6}). In the spectra the component C has more spectral weight than the D, reflecting relative small ionicity of the tetravalent ground state of this compound. Based on the previous reports [19] the shoulder B is assign to a Ce^{3+} impurities. The weak feature A in the pre-edge region is expected by a dipole-forbidden 2p_{3/2} 2p_{1/2} to 4f transition, which is a consequence of 5d admixtures to the 4f state [20]. Therefore, the present Ce L – edge spectra reflect a typical feature of CeO_{2} thin films and matches well with the reference spectrum of Ceria powders. However, we have not observed any significant changes in the spectra with increasing the Ni
concentrations, indicating that spectral features of Ce L edge spectra are not affected by the Ni implantation.

To further understand the effect of Ni implantation on the magnetic properties of CeO\textsubscript{2} thin films, systematic, magnetization measurements were performed at RT and presented in the Fig. 4. It is evidenced from the Fig. 4 that all the samples show RT ferromagnetic nature. The 2 at.% Ni implanted sample shows maximum saturation magnetization. Further increase in the Ni concentrations leads to decrease in the net magnetization; additionally, the loop is also open at higher field values for the higher Ni concentration implanted CeO\textsubscript{2} thin films. The higher saturation magnetization in the 2 at.% Ni implanted sample may arise due to direct exchange interaction among the neighbor Ni ions in the CeO\textsubscript{2} matrix, as their concentration is low. Similar larger saturation magnetization has also been observed in the previous reports [21]. Further increase of Ni concentrations leads to formation of secondary phases of Ni oxide in the CeO\textsubscript{2} matrix, as evidenced by XRD and Ni L-edge NAXAFS measurements. Such mixed phases in turn leads to formation of centers of competing magnetic phases, like: antiferromagnetic Ni oxide phases and ferromagnetic pairs of Ni ions [22] resulting net degradation in the overall magnetization. Such competing effects may be responsible for the observed decrease in the net magnetization in the higher Ni concentration implanted CeO\textsubscript{2} thin films.

CONCLUSION

From a procedural point of view, we illustrate that how the ion implantation facility. Mayora Varshney, Aditya Sharma and Hyun-Joon Shin would like to acknowledge the financial support by the Basic Science Research Program (No. 2008-0062606, CELAC-NCCR) through the National Research Foundation of Korea (NRF) and by the Converging Research Center Program (NRF-2014M3C1A8048817) through the Ministry of Science, ICT and Future Planning, Korea.

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BIOGRAPHY

Dr Hyun-Joon Shin is a senior beam line scientist at Pohang Accelerator Laboratory and adjunct professor at Department of Physics, Pohang University of Science & Technology, Pohang-South Korea. His area of research interest is the X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, X-ray SpectroNanoscopy investigations on the oxide nanoparticles/nanorods, photocatalyst materials, polymer materials, bio-composite materials.

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