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RESEARCH ARTICLE

Synthesis and characterization of self organized SiO_2 nano pillar with MnO as the magnetic tip.

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Abstract

Self organized SiO_2 nanopillar with MnO tip have been synthesized over Si substrate by annealing the substrate after putting drop of $MnCl_2$ (in C_2H_5OH and H_2O) over its surface. The controlled growth of nanopillars has been achieved by annealing as sampled Si substrate at 940 ^oC in Ar and H_2 gas environment (Ar =150 ml/min, H_2 =75 ml/min) for 2 hour. Synthesized nanopillars are vertical over the silicon substrate. Energy dispersive x-ray (EDX) analysis shows that the pillar structures are formed of Si, O and Mn, wherein the catalyst Mn has been found in the form of MnO at the tip of the nanopillar, inferred from the EDX, X-ray magnetic-circular dichroism (XMCD) and near edge x-ray fine structure (NEXAFS) analysis. HETEM analysis shows the tip as well as the pillars are amorphous. The MnO tip has magnetic nature as concluded by XMCD studies of the samples. Spectral features of Mn K-edge EXAFS reveals that Mn is in 2+ state and coordinated in tetrahedral symmetry.

Introduction

The synthesis of magnetic nanodots either in matrix or onto substrate has been an interesting subject because of increasing demand of magnetic recording media and magnetic devices (1, 2). Several groups have fabricated magnetic nanodots (3-5) and many methods have been adopted to fabricate nanodots arrays such as, ion beam (6) or indirect (7-9) lithography and interferometric laser (10, 11). Ferromagnetic nanodots arrays have been investigated by numbers of researchers.(12, 13) also manganese oxide has attracted a great deal of interest due to the complex interplay of orbital, charge, and spin order (14). However, the methods used for production of nanodots are expensive and painstaking. Here we present an easy method for the synthesis of ferromagnetic MnO nanoparticles at the tip of SiO_2 nanopillars. The nanopillars are self arranged over the surface of silicon with same height, and containing almost uniform sized ferromagnetic MnO nanoparticle at their tip.

Although magnetization measurements and anomalous Hall effect measurements can measure the magnetic properties, but still not a confirmed method to declare that magnetism is extrinsic or intrinsic [15]. X-ray magnetism circular dichroism (XMCD), which is the difference in core-level absorption spectra between right and left-handed circularly polarized x-rays, is an element specific probe sensitive to the magnetic polarization of each element, and therefore enables us to directly extract the local electronic structure related to the particular magnetic properties of the substituted transition metals ions [16,17].

In this letter, we report the electronic structure of MnO magnetic tip of SiO_2 nanopillars, studied by near edge x-ray fine structure (NEXAFS) and X-ray magnetic-circular dichroism (XMCD). NEXAFS and XMCD are powerful tools for understanding the electronic structural properties of solid materials. These techniques are element specific and are capable of probing the density of unoccupied and occupied state of atoms. Thus, NEXAFS and XMCD play crucial roles in determining the valance states of atoms in solid state due to its simplicity and universal applicability.

Here, we also present and discuss the study of NEXAFS and XMCD spectra of Mn $L_{3,2}$ and K –edges for Manganese oxide magnetic tips on SiO_2 nano pillars.

Experimental:-

Boron doped, p-type Si (100) wafers cleaned by acetone and 5% hydrofluoric acid followed by heavy rinse under running deionized water, was dried first, and then after putting a small drops of manganese chloride ($MnCl_2$ 99%) in ethanol and water in 9:1, were placed in a quartz tube in a high temperature furnace. Synthesis of SiO_2 nanopillars was carried out at 940^{o}C temperature in argon gas environment, using hydrogen gas as the reducing agent (Ar:H_2 2:1) for 2 hours annealing time. These samples were examined with field emission scanning electron microscopy (FESEM), High resolution transmission electron microscopy (HRTEM), Extended X-ray Absorption Fine Structure (EXAFS) and X-ray magnetic circular dichroism **(**XMCD**).** The NEXAFS measurements of these samples along with the reference compounds of MnO_2 and MnO at Mn *K* -edge was performed operating at 2.5 GeV with a maximum storage current of 200 mA. This beamline is monochromatized by a double-crystal Si (111) monochromator detuned from 20 to 30%, to suppress higher-order harmonic content from the beam. All the scans were made in transmission mode with nitrogen-argon gas-filled ionization chambers as detectors. The Mn *K*- edge energy was calibrated using the first inflection point of the edge region of a metallic Mn foil. The resolution of the monochromator was about 1.5 eV in the energy range studied. The 2A MS undulator beamline was utilized to carry out Mn $L_{3,2}$ –edge NEXAFS and XMCD measurements. This beamline has an elliptically polarized undulator with greater than 90% degree of circular polarization. Present measurements were done at RT with the base pressure better than $3x10^{-10}$ Torr and in the total electron yield (TEY) mode with resolutions of 0.10 and 0.15 eV, respectively, for Mn L -edges. The XMCD spectra were taken for a fixed helicity of the light by reversing the applied magnetic field (0.8 T) for each h□. The spectra were normalized to incident photon flux. The data is normalized and processed using Athena 0.8.056/IFEFFIT 1.2.11.

Results and Discussion:-

FESEM image of nanopillars obtained at 940^{o}C annealing the sample for 2 hour is shown in fig. 1. The nanopillar structures are self organized, standing vertically over the silicon substrate. The tip diameters of the pillars range from 50 to 100 nm with their base diameters from 100 to 200 nm, the height of all the nanopillars have been found approximately same and about 200 nm above the silicon surface.

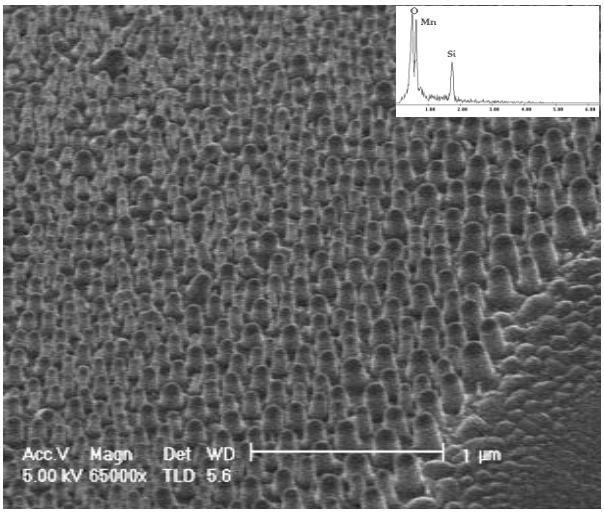

Figure 1:-Field Emission Scanning Electron Microcopy (FESEM) image of the highly organized SiO_2 pillars over silicon substrate at viewing angle 45^o. The upper right inset is EDX Pattern installed in the FESEM.

From the corresponding EDX spectrum (inset of Fig. 1) silicon, oxygen and manganese are indicated as the constituent of the nanopillars. We performed the EDX analysis for point areas at the tip (black part at pillar) and at pillar (bright part). The elemental composition of the silicon and the oxygen was in ratio (Si:O=1:2), and manganese and oxygen also in approximately ratio 1:1. It is concluded conclude from these EDX results, that MnO exist at the tip of SiO_2 pillar. These EDX analyses were performed at viewing angle 45^o to avoid the contribution of the

substrate silicon. Structure analysis was carried out using high resolution transmission electron microscopy (HRTEM). Fig. 2 is a typical HRTEM image of the nanopillar, showing amorphous structure a pillar. Further the selected area diffraction pattern (SADP) of the tip (dark region in HRTEM image) is shown in inset of Fig 2. Again from SADP it is clear that the tip of the nanopillar is amorphous.

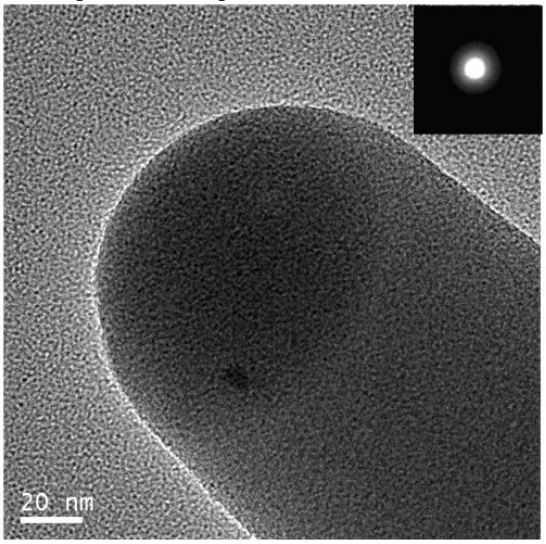

Figure 2:-High resolution transmission electron microscopy (HRTEM) image of a nanopillar. The inset shows SADP of the tip of nanopillar, indicating amorphous structure.

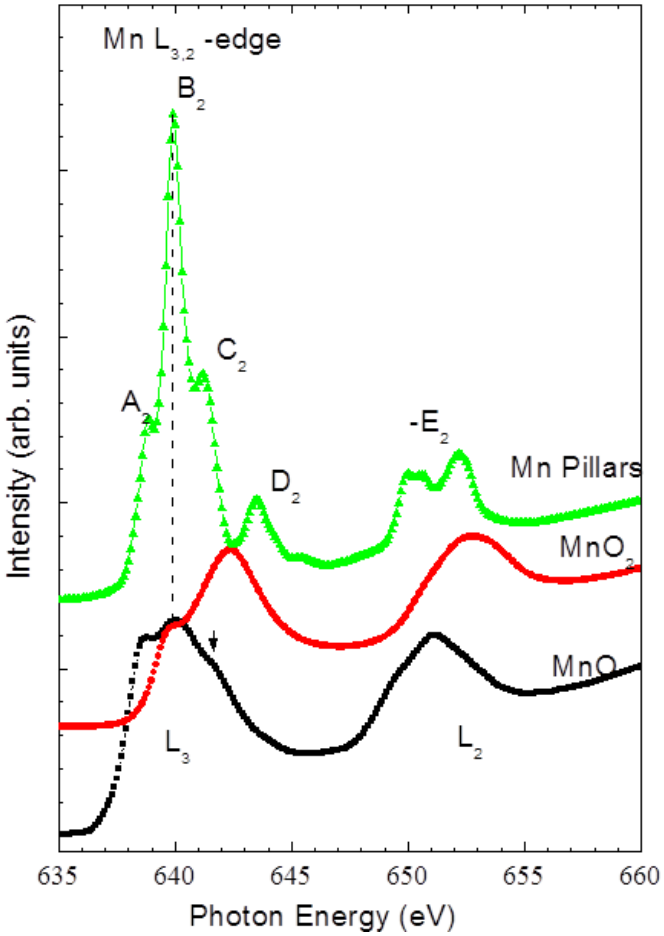

Figure 3:-Mn $L_{3,2}$ -edge for MnO Magnetic tip on SiO_2 nano pillars with reference spectra MnO and MnO_2.

Quantitative structural information about the metal environment in complex materials can be obtained from extended X-ray absorption fine structure (EXAFS) spectra, whereas X-ray absorption near edge structure (XANES) can provide electronic and structural information around each atom. In the present study, we have examined the valance state and coordination state of implanted nickel atoms in quartz matrix by X-ray absorption fine structure (XAFS) spectroscopy, both by EXAFS and XANES techniques.

The NEXAFS at Mn $L_{3,2}$ edge determines the 3d occupancy of the Mn ions and hence provide some information on the valence states of the Mn ions in the compounds. In general, valance state of 3d transition metals can be precisely characterized from NEXAFS of $L_{3,2}$ –edge. The 3d transition metals also exhibit a valance-specific multiplet structure and chemical shift towards higher energy losses with increasing oxidation state [18, 19]. The Mn $L_{3,2}$ -edge NEXAFS of the sample with reference compounds MnO and MnO_2 are shown in Fig. 3. These spectra are due to Mn 2p → 3d transition. The intensity of this line can be regarded as measure of the total unoccupied Mn 3d states. The spectra show two broad multiplet structures, L_3 and L_2 separated by spin-orbit splitting. As is evident from the figure, the L_3 region comprises spectral features (A_2-D_2) and resembles with MnO (Mn^{2+}) spectral feature indicating +2 valance state for Mn. The spectral features (A1-A3), are assigned to Mn t_{2g} and e_g subbands, respectively [18].

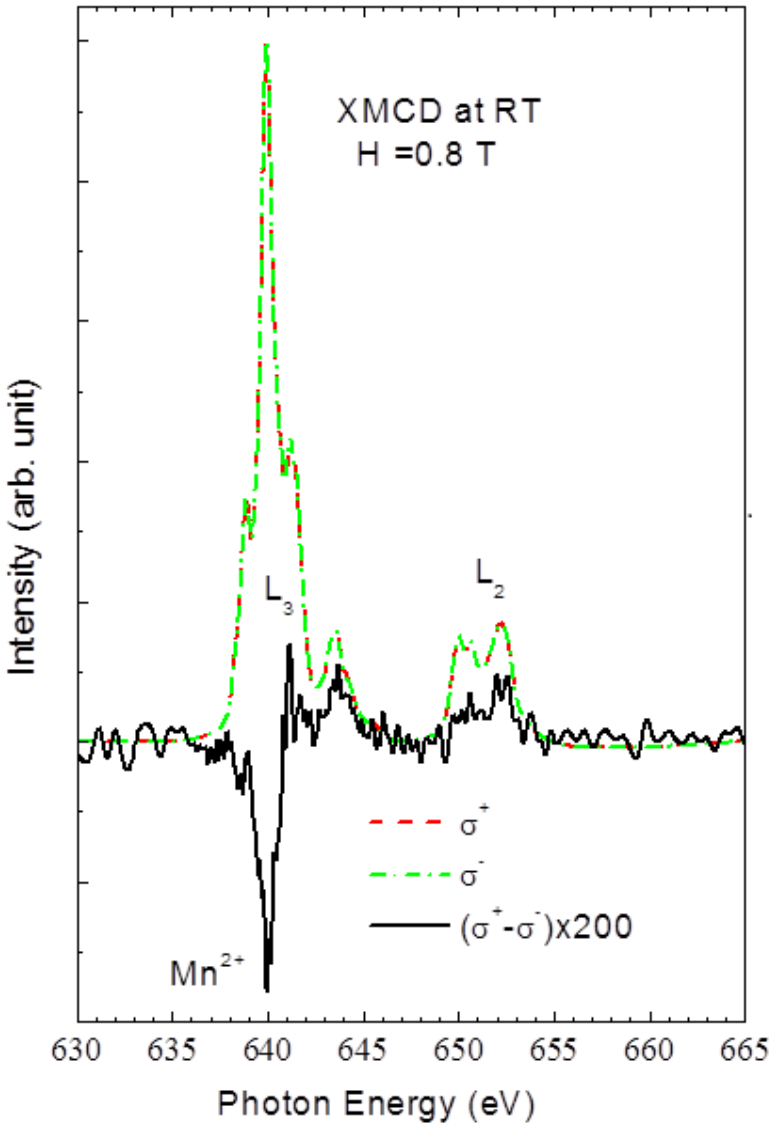

Figure 4:-Mn $L_{3,2}$ XAS and XMCD spectra of MnO tips at room temperature, obtained with photon helicity parallel (□ +) and antiparallel (□-) to the magnetization.

Fig. 5 shows the normalized XANES spectra at the Mn K-edge of sample along with reference compounds MnO2 and MnO. The pre-edge peak A1 was assigned to the direct quadrupole transition from 1s to the empty Mn 3d states [20-23].

The XMCD measurements were performed to probe the element-specific local magnetic interactions by detecting NEXAFS at the Mn L3,2 edge by reversing the applied magnetic field for a fixed photon helicity. The XMCD signal in Fig. 4 is the

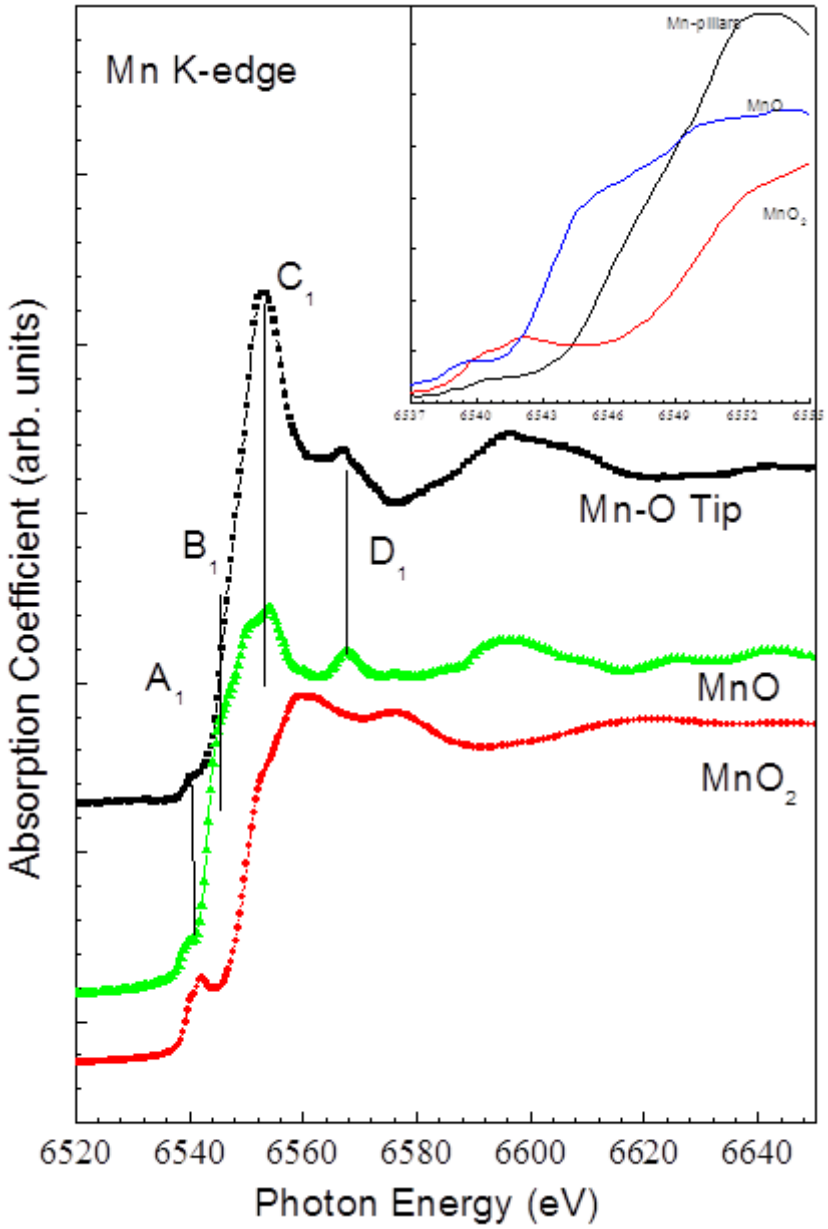

Figure 5:-Normalized Mn K-edge for MnO pillars with reference spectra MnO and MnO_2. Inset show a closeup of the pre-edge feature of the same.

difference between NEXAFS spectra recorded for the parallel (□ +) and antiparallel (□-) alignments of the photon helicity with the applied field. As evident, a clear XMCD (□ +-□-) with a negative sign at hν =640 eV confirms that Mn2+ ions are responsible for ferromagnetic ordering at RT. Based on XMCD sum rules, the vanishing intensity of the XMCD signal at L2 edge usually denotes the presence of large orbital magnetism

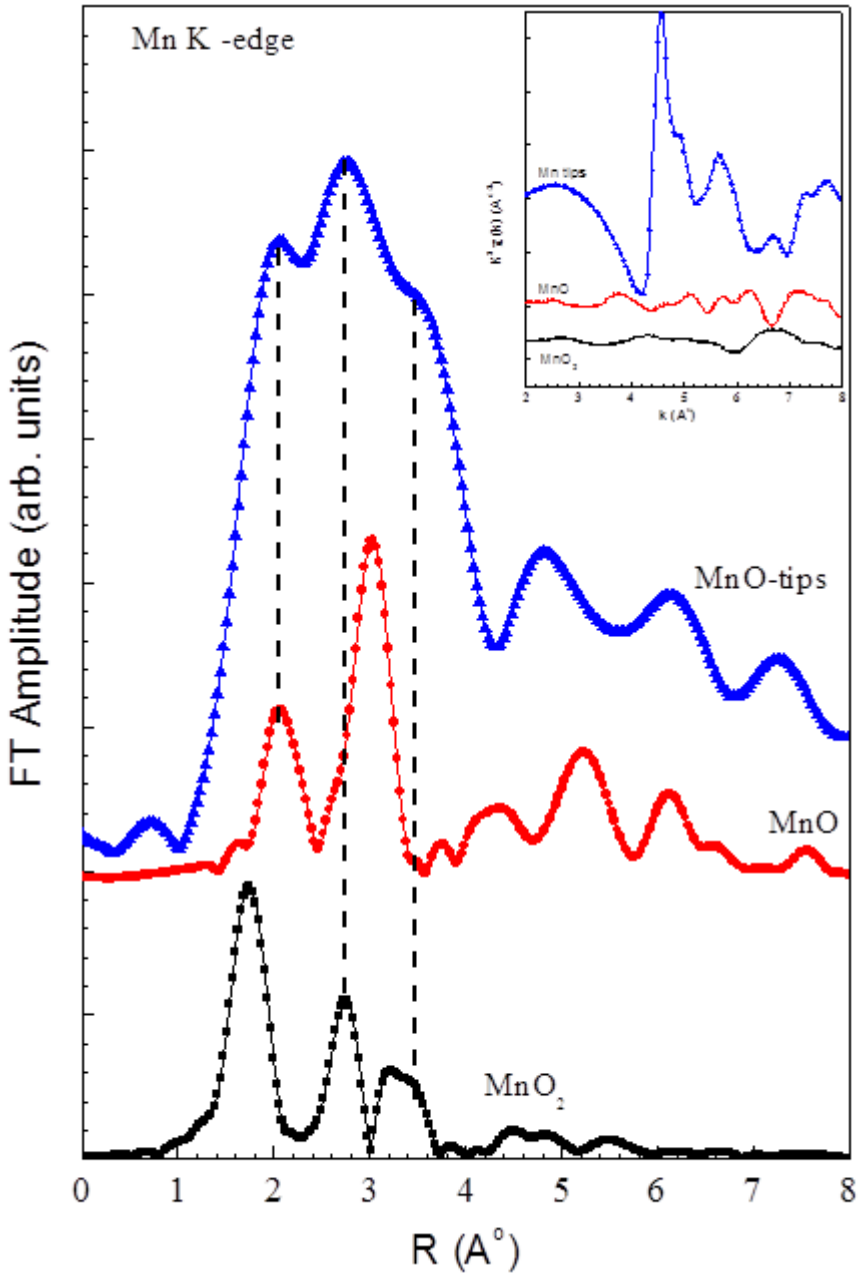

Figure 6:-Real space, k-space and q-space plots for the Mn-O magnetic tips on SiO_2 nano pillars.

[24]. This result shows that Mn is present in the divalent state which enhances carrier density apart from a highly correlated state of ferromagnetic ordering.

Conclusion:-

MnO nano tips are synthesized successfully over SiO_2 nano pillars. XAS measurements show that Mn exists as Mn2+ and in Mn is in tetrahedral symmetry with oxygen atoms, as predicted by pre-edge formation. XMCD measurements show MnO tips as ferromagnetic at room temperature. FT also predicts the environment of Mn atom in the neighborhood of oxygen.

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