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Transition metal oxides in etched ion tracks: Surface morphological studies

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ABSTRACT

Transition metal oxide (TMO) nanoparticles comprising of different magnetic properties, have been inserted in ion tracks which have been created by swift heavy ion bombardment of the SiO_2/Si substrate and further etched by hydrofluoric acid. To study the surface morphology of the system, pore structure (diameter, shape, size and depth), pore volume and surface area before and after filling of TMOs, atomic force microscopy (AFM) and Brunauer–Emmett–Teller (BET) techniques have been used. These TMO filled structures have been subjected to perpendicular magnetic field to study the alignment of the metal oxide particles. In this paper, the surface morphology of TMO based nanostructures is being reported corroborating the findings with vibrating sample magnetometer (VSM) and transmission electron microscopy (TEM) studies.

1. Introduction

Nanostructured materials obtained using swift heavy ions have a wide range of possibilities for application in numerous fields. Moreover, because of their paramount importance in microelectronic devices, silicon and silicon dioxide are important materials and still promising candidates for many modern micro and optical applications [1–3]. A significant number of investigations have been devoted to the study of interaction of swift heavy ions with dielectric surface layer. It is a method of surface modification where the surface properties significantly change while the bulk properties are retained. The morphology of the surface tracks depends upon the ion energy as well as the physical properties of the irradiated material [4–7]. These latent ion tracks when etched by a suitable etchant and subsequently filled with different fillers, create a new class of electronics based on the TEMPOS (Tunable Electronic Material with Pores in Oxide on Silicon) structure. These TEMPOS structures have been used in different fields and applications [8–10]. The techniques of scanning probe microscopy (especially AFM) provide the unique opportunity of characterizing the surface before and after ion beam exposure since, depending upon the sensitivity of the solid, the degree of disorder can range from point defect to continuous amorphized zone along the ion trajectory. Different features of these types of materials have been reported previously [7–14].

The structural characterization techniques for porous structures cover a broad range of physical methods. The morphology related techniques (such as gas adsorption–desorption, atomic force microscopy, electron microscopy and X-ray scattering) give complete information about the porous structure.

The ion track based nanostructure (TEMPOS) has the potential to be used as a magnetic sensor [22,28]. In the present paper, studies on etched ion tracks filled with different transition metal oxides having different magnetic properties are being reported. Transition metal oxides constitute one of the most interesting class of solids, exhibiting a variety of structures and properties [13]. These interesting properties arise due to the outer d electrons of the transition metal ions. Without an external magnetic field, these particles form clusters due to the particle–particle interaction while, when an external magnetic field is applied, they tend to form a chain like structure along the magnetic field direction and this tendency becomes more evident with increasing field strength [15–19]. Also, the unpaired spins of the dangling bonds created during the ion irradiation process interact with the external field to yield the quasiferromagnetism in the damage associated silicon [20]. So, when these ion tracks are filled by the TMOs having different magnetic properties, they behave independently having different surface and inner configuration. Surface morphology study of these structures has been done with BET and AFM. The crystallite size of the synthesized TMO nanoparticles has been determined by XRD and TEM. Vibrating sample magnetometer (VSM) measurement has given the detailed account of magnetic properties (Ms, coercivity) of the TMO particles and the nanostructures (TEMPOS).

The pore volume and surface area of the porous and filled material using BET has been reported earlier [21–23]. The BET method has been employed to correlate the pore volume and area with the AFM measurements.

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2. Experimental studies

Ion tracks were created by the bombardment of Au^{26+} ions of energy 350 MeV and fluence of $10^8/cm^2$. The thickness of dielectric layer (SiO_2) and silicon substrate were 100 nm and 375 μm, respectively. Latent tracks created by this process were etched by 4% hydrofluoric acid for 14 min which created parallel open tracks on the substrate. Nanoparticals of different transition metal oxides were synthesized by different methods; Fe_3O_4 by the method given by Racuciu et al. [24], NiO by the method given by Cai et al. [25], Co_3O_4 by the method given by Yang et al. [26] and Mn_3O_4 by the method given by Shuijin Lei et al. [27]. These synthesized nanoparticals (water as a carrier fluid) were inserted in the ion tracks of SiO_2/Si substrate. A thin layer (~μm) was deposited on the top surface of the substrate.

The synthesized nanoparticles were examined by powder X-ray diffractometer (D8 Advance) with CuK_α radiation at room temperature and HRTEM (Technai G^2 300KV). The AFM images of the empty and the filled TEMPOS structures were taken by Veeco instrument (2002) in contact mode. The BET measurements were done with Gemini-V2.0 instrument (Micromeritics Instrument Corp.). Both the pore volume and surface area were calculated from the isotherm according to the BET theory. Furthermore, the magnetic properties of the system (that affect the surface morphology) were measured by VSM (Microsense, ADE-Model E V9).

3. Results

3.1. XRD and TEM analysis

The XRD patterns [28] of the transition metal oxide nanoparticles have given the crystallite size (employing the Scherrer relation) of Fe_3O_4, NiO, Co_3O_4 and Mn_3O_4 nanoparticles to be ~10, ~13, ~12 and ~11 nm, respectively.

Fig. 1 shows the TEM images of the transition metal oxides nanoparticles which clearly indicate the chain like structure of nanoparticles, especially in Fe_3O_4 particles. The nanoparticles inserted in the tracks can easily make chain like structure inside the tracks in the presence of a magnetic field. Also, micrograph 1(a) indicates that the particle size ~10 nm. Fe_3O_4 nanoparticles adopt a regular spherical shape and they arrange to give aggregates of spherically shaped particles. This is attributed to the magnetic interaction between the nanoparticles. Micrograph 1(b) reveals the presence of a large number of NiO particles with hexagonal shape and size ~13 nm. Inset in the figure shows the selected area electron diffraction pattern of the nanoparticles. The appearance of strong diffraction spots rather than diffraction rings confirmed the formation of single crystalline cubic nickel oxide. From the micrograph 1(c) one can get the size of Co_3O_4 to be nanoparticles ~12 nm and of Mn_3O_4 nanoparticles (Fig 1d) ~11 nm. As discussed by Morup et al. [29], nanoparticles of ferromagnetic and ferrimagnetic materials with dimensions ~10 nm, can have magnetic moments larger than 10,000 Bohr magnetons leading to dipole interactions between the nanoparticles which can have a significant influence on the magnetic properties and the shape of the nanoparticles.

3.2. AFM studies

AFM studies have been done with the empty and TMO nanoparticles filled ion track substrates. Fig. 2 shows the ion tracks on the dielectric layer. From Fig. 2(a), the number of tracks per unit area has been calculated to be $\sim 2 \times 10^8/cm^2$ (comparable to the fluence). This reiterates the fact that every ion hitting the SiO_2 surface leaves a damaged zone which can be etched to get well defined tracks. Fig. 2(b) shows the 3D view of the same track and 2(c) is the 3D view by SPIP software which shows the shape of tracks is conical. Note that since the tracks are conical, the probe dimension

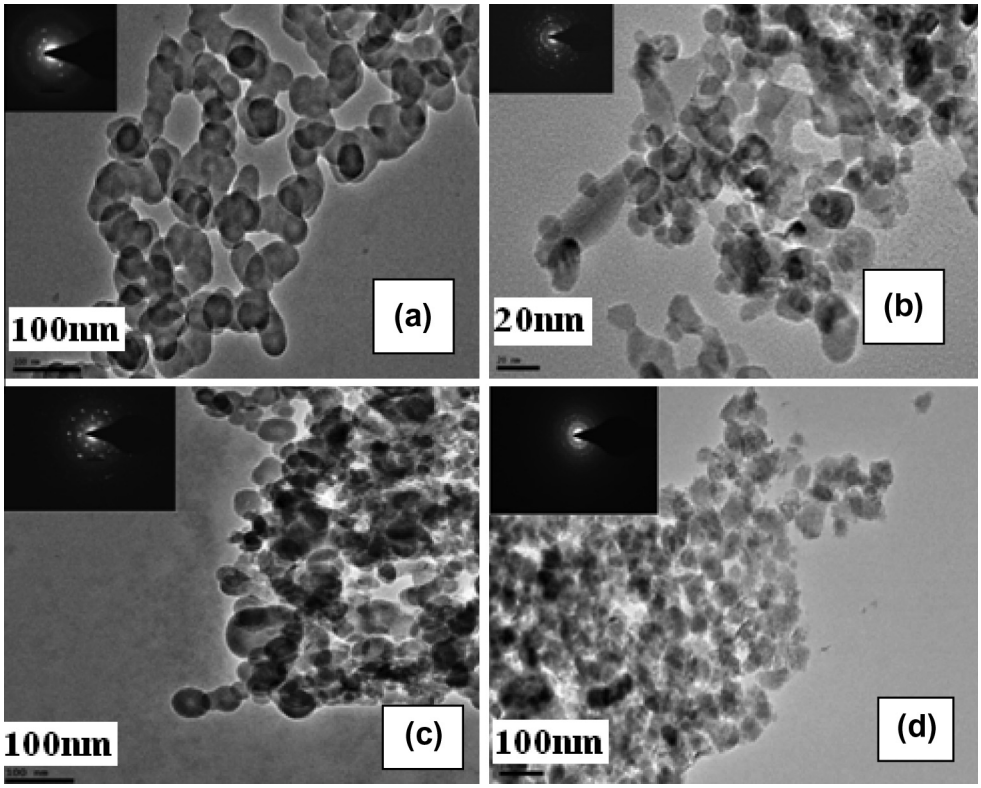

Fig. 1. TEM images of magnetic nanoparticles; (a) Fe_3O_4, (b) NiO, (c) Co_3O_4 and (d) Mn_3O_4.