

Chapter 25

Ion Track Based Novel Nanostructures: A Step Towards Magnetic Nanosensors

A. Chandra and S. Rawat

Abstract Injection of accelerated ion beam into a target specimen offers a valuable tool for altering its physical properties in a controllable manner. One of the major applications of this type of materials is the obtaining of a novel structure, namely, Tunable Electronic Materials with Pores in Oxide on Silicon (TEMPOS) for device fabrication. In the TEMPOS structure, swift heavy ions (SHI) create ion tracks in dielectric layer on semiconductor. Insertion of suitable materials (sensitive to light, gas, humidity, organic and inorganic vapors etc.) in these ion tracks can give multi-parametric sensors in a small area. The high aspect ratio of the TEMPOS structures results in a fast response time and high sensitivity and making it a probable candidate for sensor fabrication. The TEMPOS structure itself has a quasi-ferromagnetic property and inserting transition metal oxides (TMOs) nanoparticles inside the tracks makes it sensitive to magnetic properties.

Keywords Swift heavy ions • Ion tracks • Transition metal oxides

25.1 Introduction

Nanostructured materials offer opportunities for observing new phenomena and processes which, owing to the dimension, are not observed at the macroscopic level. They also exhibit novel and improved physical, chemical and optical properties. Their potential technological applications in various areas such as electronics, optics, magnetism, energy storage materials, biomedical sciences and electrochemistry result in a huge interest in them. It is well known nowadays that properties of materials on a nanoscale can be quite different from their microscopic

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counterparts. One of the reasons includes the increased surface to volume ratio which enhances the influence of surface properties.

Ion irradiation is considered to be a tool for creation and tailoring of such new materials with novel properties because of the high energy density deposited per incident ion and the capability of such a violent process to drive the solid far from the equilibrium. In metals, damage creation occurs when the electronic energy loss exceeds a certain threshold value, which may vary from metal to metal. Thus, swift heavy ion (SHI) induced defect production and atomic motion in metals have stimulated a great interest in understanding the interfacial mixing across the metal/metal interfaces to produce novel materials and phases [1, 2].

Using ion irradiation of dielectric layer on a Si substrate, a novel family of electronic structure TEMPOS (Tunable Electronic Materials with Pores in Oxide on Silicon) has been realized. In this new type of nanoelectronics, A/B bilayer structures have been used, with B being a Si substrate and A being a swift heavy ion irradiated insulating layer such as SiO_2 , SiON or a polymer, which has been etched and filled with some conducting material. The behaviour of these structures is determined by the material and the thickness of a dielectric layer, the length, shape, areal distribution of the etched tracks, distribution of the inserted material within these tracks and also by the type of Si substrate. These structures may exhibit properties of tunable resistors, capacitors, diodes, double-diodes, transistors, logic gates etc. As the TEMPOS structures are influenced by physical and chemical parameters, they also act as sensors [3–13].

Transition metal oxides (TMOs) with partially filled orbitals have strong electronic correlation. TMOs constitute an interesting class of solids as they exhibit a variety of structures and properties. While bulk Fe_3O_4 (spinel) and Mn_3O_4 (spinel) are ferromagnetic, NiO (rocksalt) and Co_3O_4 (spinel) are anti-ferromagnetic. It must be noted that the nanoparticles of these TMOs are super-paramagnetic in nature. These nanoparticles represent a broad class of materials that have been studied extensively not only because of their interesting catalytic, electronic, and magnetic properties, but also because of a wide range of their potential applications [14], such as magnetic resonance imaging [15], solar cells [16], and heterogeneous catalysis [17, 18]. Without an external magnetic field, these particles form clusters due to the particle-particle interaction. However, when an external magnetic field is applied, they tend to form a chain like a structure along the magnetic field direction and this tendency becomes more evident with the increasing field strength. This property makes them suitable for insertion in the ion tracks, since with the application of magnetic field, one can tailor the chain length in the field direction.

25.2 TEMPOS Based Sensors

25.2.1 Humidity Sensor

TEMPOS structures have been used as humidity sensors by inserting them into ion tracks polymer electrolyte and semiconductor-dispersed polymer electrolytes

as sensing elements. PEO:NH₄ClO₄ dispersed with ZnS, PbS and CdS are mixed ion + electron conductors. Inserted in the ion tracks, being predominantly proton conductors, their impedance decreases as relative humidity increases. The sensing behavior depends on the material inserted, the magnitude, and the frequency of the applied signal. Tracks act as pores of chemisorptions which lead to charge transfer between material inserted in tracks and the moisture. The most prominent merit in using ion tracks in SiO₂ as a humidity sensing material is its compatibility with the current microelectronics [11].

25.2.2 Ammonia Gas Sensor

The gas sensing behaviour of the TEMPOS structure depends on the material used, the method of preparation and the resulting microstructure. The PEO: NH₄ClO₄ polymer electrolyte has been chosen because of its proton conduction and reactivity towards H⁺ ion containing impurities. The TEMPOS structure in which ion tracks have been filled with 5 wt% Cd (Pb or Zn) salt dispersed in PEO:NH₄ClO₄ (96:4) shows that with the increase in the ammonia solution concentration, there is the decrease in resistance. The impedance change takes place over a wide range of ammonia concentrations [12].

Earlier, sensors for temperature, pressure [19], electrolytes [20] etc. have been fabricated using nanotubule structures.

25.2.3 Magnetic Sensor

Magnetic sensors can be classified according to low, medium and high field sensing range. Devices that detect magnetic fields <1 μG are known as low field sensors, those with a detection range of 1 μG–10 G are Earth's field sensors and detectors that sense fields >10 G are referred to as high magnetic field sensors. They detect changes or disturbances in magnetic field that have been created or modified. From them, the properties such as direction, presence, rotation or induced electrical currents can be studied [21–25].

It has been suggested that the unpaired spins of dangling bonds created during the ion irradiation process interact to yield the quasiferromagnetism in the damage associated silicon [26]. It has been shown by Hack et al. that annealing spark processed-Si removes the ferromagnetic behaviour in an irreversible manner, while at the same time, dramatically reduces the number of dangling bonds. It is therefore, being suggested that dangling bonds also contribute to the ferromagnetic behaviour in the quasiferromagnetic materials investigated in the present study. Note that the dangling bonds in the present case have also been substantially reduced by etching. Inserting transition metal oxide nanoparticles inside the ion tracks makes the corresponding insulator anisotropically magnetic along the track

in the TEMPOS structure. Without any applied magnetic field, these structures behave as paramagnetic materials. Upon application of the field, TMO filled ion tracks will behave according to the inserted material's property. This behavior may also be influenced by the paramagnetic properties of Si/SiO₂ substrate. The potential of TEMPOS structure as an earth magnetic field sensor (1G–5G) has been explored by filling etched ion tracks with TMO nanoparticles and the change in the I–V behavior in the presence of magnetic field has been studied.

25.3 Experimental

In the present study, the TEMPOS structure has a Si substrate (thickness $\sim 375\ \mu\text{m}$) and a swift heavy ion irradiated dielectric layer of SiO₂ (thickness $\sim 100\ \text{nm}$). The dielectric layer has been irradiated by 350 MeV Au²⁶⁺ swift heavy ions. The latent tracks thus obtained have been etched by 4% hydrofluoric acid for 14 min to create parallel open tracks of diameter $\sim 20\ \text{nm}$. Electrical contacts have been made by two thermally evaporated metal electrodes on the top surface of Si/SiO₂ substrate. Different transition metal oxides in aqueous medium have been inserted in these etched ion tracks. A thin layer ($\sim 4\text{--}6\ \mu\text{m}$) of TMO fluid has also been deposited on the surface of the dielectric layer. Figure 25.1 shows the schematic representation of TEMPOS structure.

When the TMO nanoparticles (in aqueous carrier fluid) filled TEMPOS structures are placed in a magnetic field, the magnetic particles in the fluid change their orientation according to the field direction. It has been observed that the best alignment of magnetic domains is in the parallel magnetic field direction (parallel to the ion tracks), as shown in Fig. 25.2 [31]. Thus, only the parallel field measurement have been carried out with TMO filled TEMPOS structure. They give different I–V behavior for various TMO nanoparticles depending on the magnetic and electrical properties of the magnetic fluid.

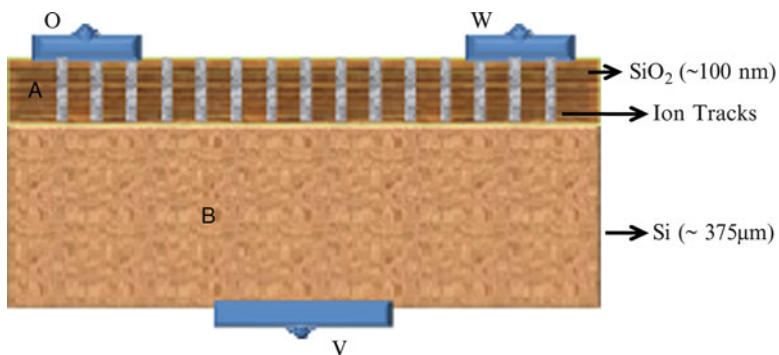


Fig. 25.1 TEMPOS structure

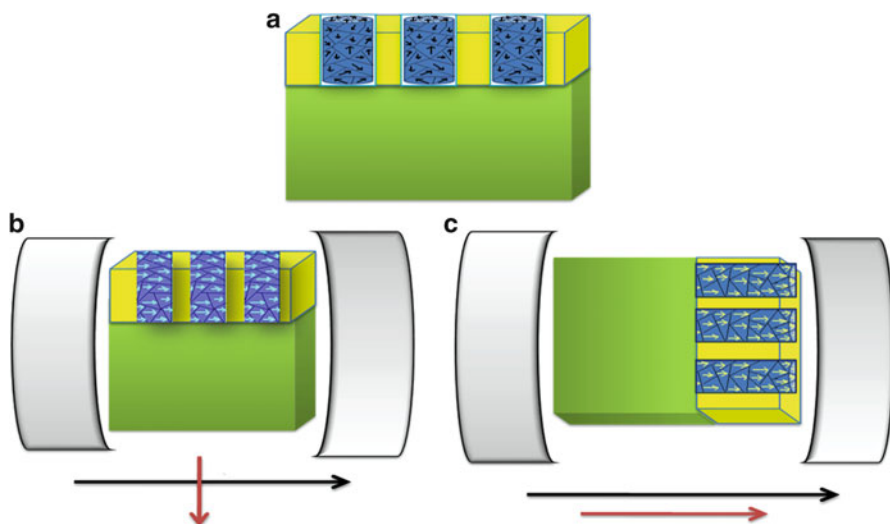


Fig. 25.2 Magnetic alignment of tiny magnetic domains: (a) without magnetic field, (b) magnetic field applied perpendicular to the track direction and (c) magnetic field parallel to the track direction

25.3.1 Synthesis and Characterization of TMO Nanoparticles

Different synthesis processes have been employed to prepare the TMOs, i.e., iron oxide using the method offered by Racuciu et al. [27], nickel oxide using the method offered by Cai et al. [28], cobalt oxide using the method offered by Yang et al. [29], and manganese oxide using the method offered by Lei et al. [30]. Distilled water has been used as a carrier for insertion of these oxides in the ion tracks. Nanoparticles of Fe_3O_4 , NiO , Co_3O_4 and Mn_3O_4 have been ultrasonicated in distilled water to get dispersed magnetic fluids.

The crystallite size of nanoparticles, pH value, conductivity of the fluid and the magnetization value have been studied and reported earlier [31, 32].

Having filled the ion tracks with these TMO nanoparticles, micropore area has been calculated by BET technique (Gemini-V2.00, Micromeritics Instrument Corp.). Figure 25.3 shows the micropore area for different TMO filled TEMPOS structure. It is clear from the figure that after Fe_3O_4 insertion in the TEMPOS structure, the micropore area is the lowest. This indicates that the iron oxide is properly filled inside the tracks as compared to other TMO nanoparticles.

The saturation magnetization (measured by VSM Microsense, ADE-Model E V9) for Fe_3O_4 filled ion tracks, Fe_3O_4 nanoparticle and Si-SiO_2 substrate (empty ion tracks) is shown in Fig. 25.4.

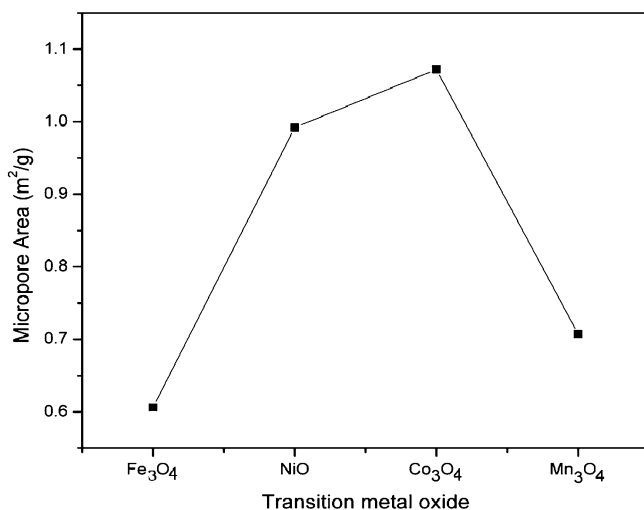


Fig. 25.3 Micropore area measurement of TMO filled TEMPOS structure

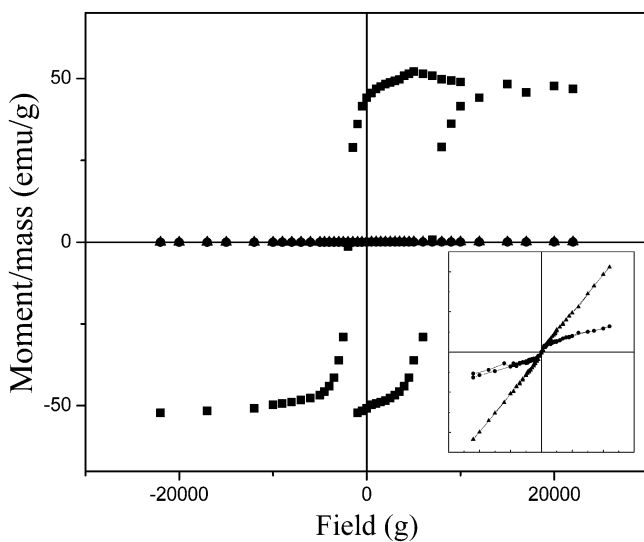


Fig. 25.4 Magnetization curves for ■ Fe₃O₄ nanoparticle, ● Fe₃O₄ inserted Si-SiO₂ substrate (*inset*) and ▲ Si-SiO₂ substrate (*inset*)

It is evident that the Fe₃O₄ nanoparticles show ferromagnetic behavior while the Si-SiO₂ substrate with ion tracks shows paramagnetic behaviour. When we insert these nanoparticles inside the ion tracks in the Si-SiO₂ substrate, it also shows ferromagnetic behavior, although the magnetization values are less than that of the free standing particles.

25.4 Results

25.4.1 Current/Voltage Characteristics

TEMPOS devices can operate in DC, with very low and high frequencies as they have higher internal flexibility. Therefore, one can design simple circuits which lead to a gain in the operation speed. In our previous work [32], we have reported the behaviour of the TEMPOS structure in the presence of magnetic field with the aim to narrow down on a system which can be used as an earth magnetic field sensor. We have studied the following systems:

1. TMO nanoparticles (Fe_3O_4 , NiO , Co_3O_4 and Mn_3O_4) filled TEMPOS structure.
2. Fe_3O_4 nanoparticles filled TEMPOS structure having different concentrations.
3. Fe_3O_4 nanoparticles filled TEMPOS structure annealed at different temperatures.

Outcome of our studies are enumerated below:

1. All the TMOs filled ion track based TEMPOS structures show change in I–V behavior. However, the iron oxide nanoparticle filled structure shows the maximum current change with the least applied voltage change.
2. Fe_3O_4 nanoparticles on the surface as well as the tracks start aligning in the external magnetic field's direction and getting saturated at 2G, while for other TMOs (NiO , Co_3O_4 , Mn_3O_4), there is a noticeable change in the I–V behavior only at 1G magnetic field, but for a higher applied magnetic field there is no significant change.
3. Furthermore, it requires magnetic field $>5\text{G}$ for saturation/alignment of magnetic moments for other TMO based sensors.

25.5 Conclusions

The results described above indicate that the iron oxide filled TEMPOS structure is the best candidate for the low field detection [32] Fe_3O_4 nanoparticle based fluid has higher conductivity (3.84 mS/cm) and magnetization value (Ms-52 emu/g) in comparison with other TMOs. As it has been presented in our previous study [31], the viscosity of the ferrofluid (Fe_3O_4) makes it easy to be inserted inside the tracks. These factors are responsible for making the Fe_3O_4 filled ion tracks as the best probable candidate for the earth's magnetic field sensor. Furthermore, it has also been shown that dilution by 50% of the ferrofluid gives the best sensitivity of the TEMPOS device in a low field.

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