Synthesis and Structural Studies on MgO Nanoparticles Suitable for Tunnel Barrier Applications

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Abstract: Magnesium oxide (MgO) nanoparticles are synthesized by a simple coprecipitation method. XRD studies reveal that nanoparticles are predominantly (100) textured with an average crystallite size of 19 nm. The relative peak intensities for (100) and (110) textured grains i.e., $I_{(100)}/I_{(110)}$ is found to be ~ 2. Scanning electron microscope (SEM) pictures of our samples indicate that our synthesized nanoparticles are spherically shaped. Due to excellent electron tunneling features of (100) textured MgO nanoparticles, our synthesis method is suitable for cost effective and simple synthesis of pure MgO nanoparticles for applications involving electron tunneling.

Keywords: Metallic oxide, MgO, Nanoparticles, chemical synthesis, tunnel barrier.

INTRODUCTION

Nanoparticles are important because of their versatile applications [1]. So far a wide variety of products using nanoparticles have been developed by researchers [1-5]. Due to large surface-to-volume ratio, nanoparticles often exhibit features which are superior to the one they exhibit in their bulk form [1]. If suitably exploited, these size dependent features can be useful for many fascinating applications. Among all, metal oxide nanoparticles are of particular importance because of their use as tunnel barrier in spintronic devices [5-7]. These tunnel barriers are normally metal oxides (e.g., MgO, Al_2O_3 etc.) which are used for the injection of spin polarized current from ferromagnetic electrodes into dilute magnetic semiconductors or graphene [7,8]. In the last few years the use of MgO tunnel barriers has gained attention due to theoretically predicted [9] and experimentally verified [10,11] huge tunnel magnetoresistance (TMR) effect. It has been shown that (100)-textured crystalline MgO films are beneficial in obtaining large TMR ratios in conjunction with Fe(100) electrodes [6,9,10]. The high TMR values for MgO(100) barriers are considered to be due to coherent spin-polarized tunneling, where the symmetry of electron wave functions plays an important role [9-11]. Thus the choice of MgO tunnel barriers for the present study is significant since the charge carriers can undergo coherent tunneling across it. The coherent tunneling enables a high spin polarization, which in turn generates a large spin signal. MgO barriers are also favorable because of their high thermal stability [6, 9-11]. Beside spintronics MgO also has other useful applications such as catalysis, ceramics, toxic waste remediation, antibacterial material refractory material etc. [12]. Clearly, a cost effective and simple synthesis procedure for making high quality MgO nanoparticles is of relevance. Among other synthesis methods, coprecipitation method is most suitable for synthesizing nanoparticles as it provide better control over stoichiometry and homogeneous mixing at the atomic scale [12].

Here, we report a simple and cost effective coprecipitation method for the synthesis of MgO nanoparticles. The structural features of our MgO nanoparticles are studied by X-ray diffraction (XRD) and scanning tunneling microscope (SEM). The XRD results show the formation of nanoparticles with an average particle size of 19 nm. XRD pattern of our particles is found to be in agreement with the standard XRD patterns of polycrystalline MgO. It is found that the sample have mainly (100) and (110) textured grains with (100) oriented MgO grains as a dominant phase. The higher percentage of (100) oriented MgO phase in our sample is very important and desirable feature for spintronics applications [9,10]. SEM images reveal that the particles are spherically shaped with significant degree of agglomeration. The presence of (100) textured MgO phase in our sample is very important to get large TMR ratios when used as a tunnel barrier in spin valves [10,11].

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EXPERIMENTAL

The starting materials for the preparation of MgO nanoparticles were magnesium-acetate-tetra-hydrate $Mg(CH_3COO)_2.4H_2O$ and dimethylformamide (DMF) in appropriate stoichiometric ratios. The calculated amount of Mg $(CH_3COO)_2.4H_2O$ was first dissolved in DMF. For this purpose 0.1 M solution of Mg $(CH_3COO)_2.4H_2O$ was prepared in 200 ml of DMF. This solution was kept on a hot plate under constant magnetic stirring at 300 °C for 2 hrs. Thereafter, the solution was cooled to room temperature. After cooling, the resulting mixture was centrifuged at 4000 rpm for 3 minutes. After the completion of reaction, a white precipitate was obtained. This precipitate was then washed several times with distilled water in order to remove the byproducts or impurities and then dried in an oven for 10 hours to obtain the final product i.e., MgO nanoparticles. To stabilize the crystal structure and remove excess water the particles were annealed at 350 °C for 10 hours in a furnace.

RESULTS

The structural quality such as crystal structure, orientation and crystallite size for nanoparticles was examined by θ–2θ scans of x-ray diffraction (XRD) patterns. Figure **1** shows a typical x-ray diffraction (XRD) pattern obtained for our MgO nanoparticles. The XRD peaks are in reasonable agreement with the standard pattern for MgO. The peaks positions are marked by their respective plane indices as obtained from the standard diffraction pattern.

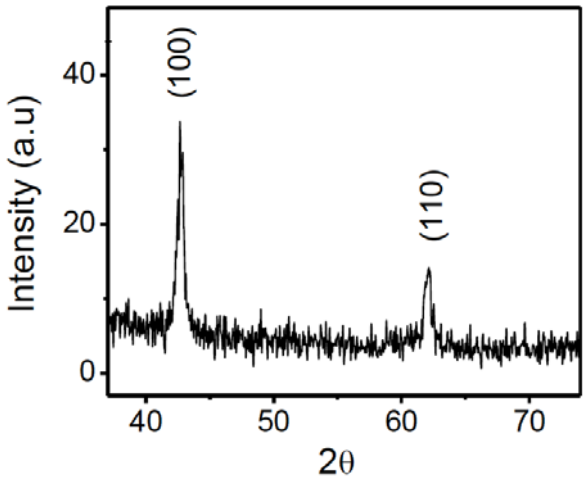

Figure 1: XRD pattern of MgO nanoparticles synthesized by coprecipetation method.

As shown in Figure **1**, the most intense peak for nanoparticles is found to be at angle 2θ = 42.6°. This correspond to the diffraction from (100) MgO planes. The average crystallite size is estimated using Scherer's formula;

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where β is the line broadening at half the maximum intensity in radians, K is the shape factor and θ denotes Bragg's angle and D denotes the mean size of ordered crystallites, which may be smaller or equal to the grain size. The shape factor is dimensionless but its value changes with the shape of crystallite. For spherical particles the value of K is about 0.9. We can apply Scherer's formula for nanoscale particles only. It is not valid for particles having size more than about 0.1 μm. The crystallite size of our sample is found to be ~ 19 nm. The information about the shape and morphology of the nanoparticles are obtained by scanning electron microscopy (SEM). Figure **2** shows SEM images of MgO nanoparticles for different magnifications. Clearly, the particles have acquired good structural uniformity with spherical shaped grains. However, significant degree of agglomeration is also noticed.

DISCUSSION

The XRD pattern indicate that the samples are polycrystalline with predominantly (100) and (110) textured MgO grains. No other peak could be found within the detection limit of XRD. The relative peak intensities for (100) and (110) textured grains ($I_{(100)}/I_{(110)}$) is found to be larger than 2. The higher $I_{(100)}/I_{(110)}$ ratio for our nanoparticles corresponds to larger proportion of (100) textured MgO phase in our nanoparticles. The presence of larger proportion of (100) textured phase in polycrystalline MgO tunnel barriers has been shown to generate enhanced TMR ratios in spin-valves [10,11]. In these devices (100) textured grains allow coherent spin tunneling for larger spin coherence lengths that yields very high values of TMR ratios [10]. Thus our synthesis method is useful for growing MgO nanoparticles particularly in applications involving electron tunneling through insulating MgO barriers [9,10] as well as in many other applications [13,14].

The particles shown in SEM images (Figure **2**) are rather large (~ 200 nm). This size range seems to be in an apparent contradiction with the one estimated by XRD data. However, the crystallite size estimated from the XRD peak using Scherer's formula should not be confused with the actual particle size. A smaller particle

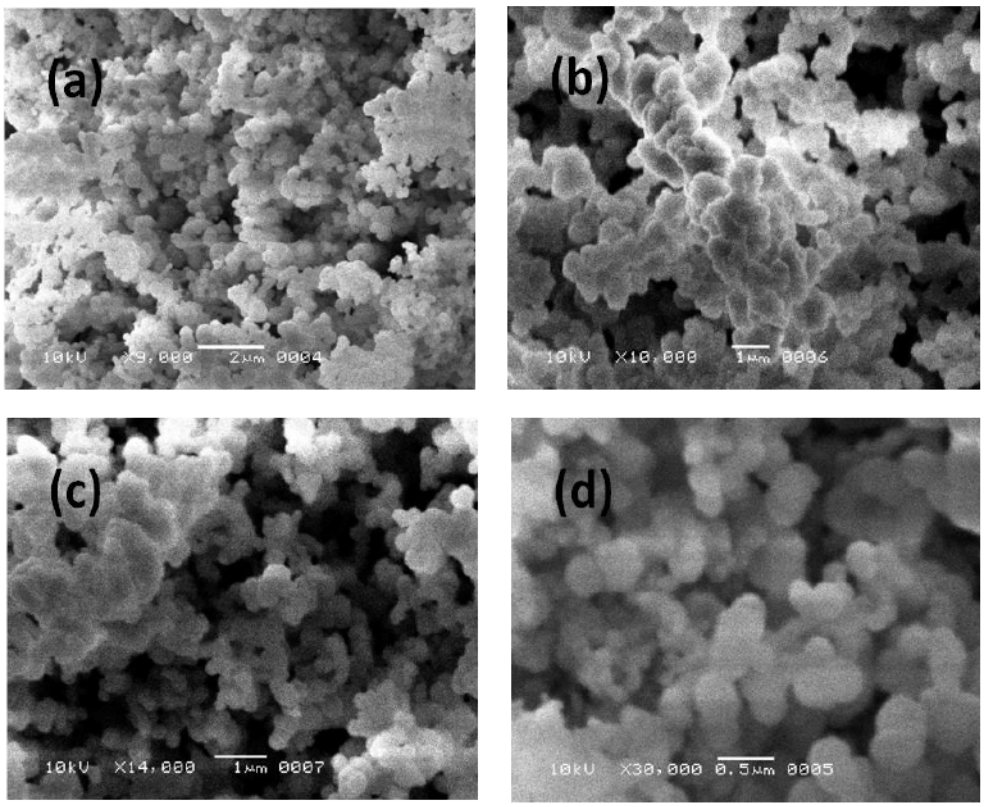

Figure 2: SEM images MgO nanoparticles under different magnifications. The latter are marked in the labeling of (**a-d**).

may have single crystal structure. However, in most cases especially the one involving chemical synthesis the resulting nanoparticles acquire polycrystalline structure [15]. These large polycrystalline particles have many small single crystalline regions or crystallites. The size of a particle estimated by XRD is normally of a crystallite i.e., a small region of a big particle and not of the whole particle. On the other hand SEM captured the images of the whole particle. Due to various technical constraints SEM is generally not considered as an appropriate tool to probe the internal structure of a nanoparticle. A better technique for this detailed analysis is transmission electron microscope (TEM). Another important point is the tendency of the nanoparticles to agglomerate in order to minimize their surface energy. As SEM studies are done by directly placing the particles on the sample holder. This has resulted in agglomeration of particles forming larger structures as clearly visible in SEM images of Figure **2a-d**.

COCLUSION

MgO nanoparticles are synthesized by a simple coprecipitation method. XRD studies reveal that nanoparticles are polycrystalline with (100) textured MgO as a dominant phase. The average crystallite size is estimated to be 19 nm from the (100) peak of the XRD pattern. Scanning electron microscope (SEM) analysis for MgO nanoparticles shows that our nanoparticles are spherical in shape. The occurrence of (100) phase of MgO is very desirable for spin-vales in order to guarantee strong enhancements in TMR values. Hence, our method is very useful for the synthesis of MgO nanostructures for future spintronic devices.

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