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Strain-induced phase-structure of Fe$_2$O$_3$ nanoparticles

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ABSTRACT

Selective synthesis of Fe$_2$O$_3$ nanomaterials with desired phase-structure is of great importance for broadening and improving their industrial applications. In this paper, the structure-phase transformation in the as-prepared samples with different annealing process is studied, trying to find a facile route to fabricate α- and γ-Fe$_2$O$_3$ nanoparticles by inducing external strain in a well control mode, which is of great importance for the design and applications of the iron oxide. The high-resolution transmission electron microscope, X-ray photoelectron spectra and Raman spectra analysis clearly demonstrate that the long-term thermal annealing and rapid thermal annealing can result in the formation of α- and γ-Fe$_2$O$_3$ confined in Al$_2$O$_3$ matrix, respectively. The magnetic properties display that the residual magnetization and coercive force values for the γ-Fe$_2$O$_3$ nanoparticles are much higher than those for the α-Fe$_2$O$_3$ nanoparticles, which supplies an enhanced magnetic route by selective synthesis of confined Fe$_2$O$_3$ nanoparticles with desired strain-induced phase-structure and paves the ways for the applications of Fe$_2$O$_3$ nanoparticles in magnetic nano-devices.

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1. Introduction

In recent years, there has been great interest in nanostructured Fe$_2$O$_3$ materials for both fundamental and practical reasons. To date, four crystalline polymorphs of ferric oxides have been thoroughly described: α-, β-, γ-, and ε-Fe$_2$O$_3$ [1]. On the basis of their different crystalline structures, each of the Fe$_2$O$_3$ polymorphs has unique biochemical, magnetic, and catalytic properties, especially at the nanometer level [1,2]. β-Fe$_2$O$_3$, possessing attractive catalytic and optical properties, is the only one in the Fe(III)—O system presenting a paramagnetic behavior at room temperature [3]. ε-Fe$_2$O$_3$ exhibits giant room-temperature coercivity and is therefore useful in advanced magnetic applications [4]. However, among the various Fe$_2$O$_3$ polymorphs, β- and ε-Fe$_2$O$_3$ are the rarest phases with a scarce natural abundance. The highly crystalline α- and γ-Fe$_2$O$_3$ that occur in nature are the most interesting and potentially useful phases. α-Fe$_2$O$_3$ has a rhombohedrally centered hexagonal structure of the corundum type with a close-packed oxygen lattice in which two-thirds of the octahedral sites are occupied by Fe(III) ions [5]. γ-Fe$_2$O$_3$ possesses a cubic crystal structure of an inverse spinel type. It contains cations in two nonequivalent crystallographic sites, i.e., the tetrahedral (A) and octahedral (B) positions [5]. In addition to its widespread use in the magnetic recording industry [6], α-Fe$_2$O$_3$ has also been used as heterogeneous catalysts [7] and solar cells [8], whereas γ-Fe$_2$O$_3$ nanostructures have been extensively examined for medical applications [9]. Recently, α-Fe$_2$O$_3$ nanoparticles in an amorphous alumina and silica matrix have been prepared by the sol-gel combustion method [10,11]. The preparation of γ-Fe$_2$O$_3$ nanoparticles is usually realized by the calcination of iron hydroxide [12,13], by the oxidation of preformed Fe$_3$O$_4$ nanoparticles, iron or organometallic iron [14—16], or using precipitation from an aqueous solution [17]. These magnetic features of α- and γ-Fe$_2$O$_3$ nanoparticles are quite different than in bulk and are a product of the smallness of particles and their structure and morphology. However, these syntheses of α- and γ-Fe$_2$O$_3$ nanoparticles is very complicated due to the need of subtle manipulation of different precursors, which, in turn, can influence the properties of α- and γ-Fe$_2$O$_3$ nanoparticles and extremely limit the applications of α- and γ-Fe$_2$O$_3$ nanoparticles in magnetic nano-devices. Therefore, it will be desirable to fabricate high performance α- and γ-Fe$_2$O$_3$ nanoparticles via self-assembled approach.

Moreover, since the advantage for the magnetism of γ-Fe$_2$O$_3$ is much better than α-Fe$_2$O$_3$, currently, it is still a hot topic in this field for the research of γ-Fe$_2$O$_3$ magnetic nanoparticles. The production of γ-Fe$_2$O$_3$ is particularly significant because the thermodynamically

metastable γ-Fe_2O_3 is the most difficult to synthesize among the iron oxides. γ-Fe_2O_3 is thermodynamically unstable and is converted either directly or indirectly (with ε-Fe_2O_3 as an intermediate product) to α-Fe_2O_3 when the temperature exceeds a threshold value [5]. Therefore, new approaches for the synthesis of stabilized γ-Fe_2O_3 phase nanoparticles as well as the investigation on their properties are of fundamental importance for the development of science and technology.

Confining the magnetic nanocrystals into a solid state matrix to form nanocomposite materials is an important mean to design magnetic nano-devices. In the case of nanocomposites consisting of γ-Fe_2O_3 nanocrystals dispersed in a solid state matrix, the matrix can stabilize the nanoparticles phase, delaying their thermal transformation into α-Fe_2O_3 [18]. The external strain can be induced during the growth process of nanoparticles confined in a solid state matrix [19,20], which has been demonstrated to be able to modify microstructures and to induce structural phase transitions in the confined nanoparticles [21,22]. By utilizing the advantages of the external strain, the crystal structure of confined nanoparticles can be well controlled by inducing an appropriate strain during the nanoparticles growth. For this purpose, we studied the structure-phase transformation in the as-prepared samples with different annealing process, trying to find a facile route to fabricate α- and γ-Fe_2O_3 nanoparticles by inducing external strain in a well control mode, which is of great importance for the design and applications of the iron oxide.

2. Experimental

Fe_2O_3 nanoparticles confined in an amorphous Al_2O_3 matrix were synthesized using pulsed laser deposition (PLD) method and thermal annealing technique. Briefly, a KrF pulsed laser beam of 248 nm wavelength with frequency of 10 Hz was used to ablate the target in an ultrahigh vacuum chamber. The targets to be laser ablated consisting of one piece of high-purity (99.99%) Al_2O_3 round target (of about 40 mm in diameter) and a square piece of high-purity (99.99%) single crystal α-Fe_2O_3 target (of about 8 mm in length) were prepared. The deposition and growth of the film on the Si substrate was carried out in a high vacuum system with a background pressure of about 1×10^{-8} Torr, with the substrate at room temperature. After deposition, the thin films were subjected to a long-term thermal annealing (LTA) process for 4 h and rapid thermal annealing (RTA) process for 60 s at 600 °C in nitrogen ambient, respectively. The deposited films structures were examined using high-resolution transmission electron microscope (HRTEM) with a JEOL 2010 microscope. The TEM electron diffraction pattern was matched against a simulated diffraction pattern for α- and γ-Fe_2O_3 generated using a TEM simulator Java electron microscopy simulation (JEMS) software, respectively [19,21,22]. X-ray photoelectron spectra (XPS) measurements were carried out with a Kratos XSAM800 spectrometer employing Al Kα radiation. The binding energies were corrected for specimen charging by referencing to the C1s peak. Raman spectra measurements are carried out with a HORIBA Jobin-Yvon Labram HR, using an excitation wavelength 514 nm. The quantum design physical properties measurement system (PPMS) with a vibrating sample magnetometer (VSM) option was used to investigate the magnetic field and temperature dependence of the magnetic moment of the deposited sample. Magnetization measurements as a function of temperature of the deposited sample were carried out, combining zero-field cooling (ZFC) and field cooling (FC) routines with an applied magnetic field of 5000 Oe in the temperature range from 5 K to 300 K. The hysteresis loops, M (H), were measured at different temperatures to determine the temperature dependence of the magnetic properties of the deposited sample.

3. Results and discussion

Fig. 1 (a) is the planar HRTEM image of the as-deposited films with its corresponding electron diffraction pattern as shown in Fig. 1 (b). Obviously, it shows void of nanoparticles and confirms that the Al_2O_3 thin film remains amorphous.

Usually, the nanoparticles formation mechanism can be explained as following: for the as-deposited film, Fe_2O_3 are dispersed in an atomic state in the Al_2O_3 matrix and all of atoms are not consumed or nucleated at room temperature. At high annealing temperatures, the Fe_2O_3 atoms have sufficient thermal energy to diffuse, find nucleation sites, and grow into nanoparticles [20,21]. Because of the thermal expansion mismatch between Fe_2O_3 nanoparticles and Al_2O_3, the Fe_2O_3 nanoparticles will suffer substantial compressive strain due to the volume expansion of confined Fe_2O_3 nanoparticles with respect to Al_2O_3 matrix [19–22]. During the LTA process, the strain may be relaxed during the formation and growth of Fe_2O_3 nanoparticles in Al_2O_3 matrix. In contrast, during the RTA process, this volumetric difference may arise from the matrix atoms not being able to move rapidly enough to accommodate the growing nanoparticle, which results in compressive strain on the nanoparticle. The strain distribution in Fe_2O_3 nanoparticles confined in Al_2O_3 matrix by RTA process is qualitatively simulated with finite element (FE) calculations, which are undertaken by using commercial software package ANSYS [19,21,22]. The Young's modulus is taken to be 219 and 360 GPa for Fe_2O_3 and Al_2O_3, respectively, while the Poisson's ratio is taken to be 0.19 and 0.24 for Fe_2O_3 and Al_2O_3, respectively. Fig. 2 (a) shows the cross-sectional strain distribution for RTA Fe_2O_3 nanoparticle grown in Al_2O_3 matrix. Correspondingly, Fig. 2 (b) shows the X-Y plane strain profile of RTA Fe_2O_3 nanoparticle grown in Al_2O_3 matrix. Obviously, the growth of Fe_2O_3 nanoparticle by RTA process suffers compressive strain from the Al_2O_3 matrix. It should also be noted that the compressive strain existing at the surface of the Fe_2O_3 nanoparticle is weaker than that in the center of the Fe_2O_3 nanoparticle. This net deviatoric strain distribution may have a significant influence on the microstructure of the confined growth of Fe_2O_3 nanoparticle by RTA process.

Fig. 3 (a) shows the low magnification TEM image of the LTA Fe_2O_3 nanoparticles confined in Al_2O_3 matrix. It can be seen that a large number of Fe_2O_3 nanoparticles are formed and confined in Al_2O_3 matrix. Fig. 3 (b) presents the electron diffraction pattern of LTA Fe_2O_3 nanoparticles. The diffraction pattern is matched against a simulated diffraction pattern generated by JEMS software. By comparing the experimental diffraction pattern with the simulated one, it can be deduced that the LTA Fe_2O_3 nanoparticles presents trigonal/rhombohedral crystal structure (space group R-3cH), corresponding to the α-Fe_2O_3 phase [23]. Fig. 3 (c) displays the HRTEM image of a single α-Fe_2O_3 nanoparticle confined in Al_2O_3 matrix. Obviously, the Al_2O_3 matrix still remains amorphous after LTA process in nitrogen ambient, while a single crystalline α-Fe_2O_3 nanoparticle with spherical shape forms in Al_2O_3 matrix. The average size of the α-Fe_2O_3 nanoparticles is about 10 nm. Fig. 3 (d) shows the low magnification TEM image of the RTA Fe_2O_3 nanoparticles confined in Al_2O_3 matrix. Similarly, a large number of Fe_2O_3 nanoparticles are formed and confined in Al_2O_3 matrix and the Al_2O_3 matrix remains amorphous after RTA in nitrogen ambient. Fig. 3 (e) presents the electron diffraction pattern of RTA Fe_2O_3 nanoparticles. By comparing the experimental diffraction pattern with the simulated one, it can be deduced that the RTA Fe_2O_3 nanoparticles presents tetragonal crystal structure (space group P43212), corresponding to the γ-Fe_2O_3 phase [24]. Fig. 3 (f) presents the HRTEM image of a single γ-Fe_2O_3 nanoparticle confined in Al_2O_3 matrix. The average size of the γ-Fe_2O_3 nanoparticles is also around 10 nm. Obviously, the annealing conditions