Synthesis and characterisation of nanocrystalline iron oxides via ultrasonic spray assisted chemical vapour deposition

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Abstract. The synthesis and characterisation of nanocrystalline magnetic materials with different morphology have attracted much attention for understanding the fundamental aspects of magnetic-ordering with reduced dimensions and for possible new potential applications in data storage technology. We report here a novel synthesis route for nanocrystalline magnetite Fe$_3$O$_4$ by ultrasonic spray assisted chemical vapour deposition, in which either iron acetate or iron acetylacetonate are used as precursors. Magnetically coupled nano-grains and nano-islands of Fe$_3$O$_4$ with different size and morphology can be produced at different conditions. The structure of as-deposited and post-annealed nanoparticles was investigated by field emission gun scanning electron microscopy (FEGSEM), x-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface roughness was measured by atomic force microscopy (AFM).

1. Introduction

Magnetite (Fe$_3$O$_4$) has received much interest due to its high Curie temperature (860K) and fully spin polarised half metallic character, which can allow for spin-dependent tunnelling magnetoresistance (TMR) with quite a high efficiency [1,2]. These characteristics can potentially be utilized in the development of magnetic random access memory (MRAM) devices that operate at room temperature with high performance capabilities [3]. From the application point of view, growth of epitaxial ferrite films is desirable and epitaxy should improve the magnetic properties of the film. Moreover, an epitaxial ferrite would allow the deposition of further epitaxial or oriented layers of other materials on the ferrite, thus increasing the device-design possibilities. There have been several methods to fabricate iron oxide films, such as pulsed laser deposition (PLD) [2], oxygen-plasma-assisted molecular beam epitaxy [4], and chemical vapour deposition (CVD) [5]. Apart from epitaxial films, nanostructured magnetic iron oxides have also attracted increasing attention in recent years. It has been expected that with reducing dimensions magnetic materials can bring new potential applications such as high density recording media and bioinspired materials. Different processes for the growth and deposition of magnetic iron oxide nanoparticles and 1D materials, such as single crystalline Fe$_3$O$_4$ nanowires [6], have been reported.

In this report, nanostructured iron oxides on various substrates have been studied using a novel ultrasonic spray assisted chemical vapour deposition. Both self assembled nanocrystals and epitaxially grown nanoislands were deposited and characterized.
2. Experimental

The experimental setup is similar to the previous paper of our groups [7,8]. In this study, either iron(II) acetate or iron(III) 2,4-pentanedionate was used as a precursor. Before the deposition, 50ml-100ml diluted precursor solution (0.01-0.05M) was first delivered into a quartz glass container with a 0.5 cm diameter nozzle and an 8 cm diameter base. The base of the quartz vessel was a 0.075 mm thick polyethylene sheet, which was secured with a clamp. The vessel was then placed in a deionised water bath containing two 1.8 MHz transducers. A substrate (Si or MgO) was mounted on the bottom of a hot-plate, of which the temperature was kept constant (300-600°C) during the deposition. After the substrate reached the desired temperature, the precursor aerosol was generated from the vibration of the transducers and was delivered towards the heated substrate by the carrier gas argon. The gas flow rate used was between 3-7 l/min. The deposition time for the iron oxide was 10 to 80 minutes. The solvent in the precursor solution was evaporated before reaching the heated substrate and the precursor was subjected to decomposition to form iron oxide on the various substrates.

X-ray diffraction (XRD) measurements were made using a Phillips X’Pert x-ray diffractometer in the Bragg-Brentano geometry, with Cu-Kα radiation. All samples were observed by using field emission gun scanning electron microscopy (FEGSEM, JEOL 6330F). The determination of surface roughness as well as the size of the individual particulates was carried out using atomic force microscopy. (AFM, Digital Instrument Nanoscope III). Iron oxide nanoparticles were also characterized using transmission electron microscopy (TEM).

3. Results and discussion

Figures 1(a) and (b) show FEGSEM images of iron oxide nanograins deposited on Si (100) substrates under different magnifications. In this case, 0.05M iron (III) 2,4-pentanedioate was used as the precursor solution and the deposition time was 30 minutes. Figure 2 shows the XRD results which indicate that Fe₃O₄ (magnetite) and γ-Fe₂O₃ (maghemite) coexist to form a nanocomposite. As shown in figure 1(b), the average nanoparticle size is about 20 nm. The swirl-shaped nanograins indicate the possible magnetic coupling.

We have also studied the effect of annealing on magnetic properties, although both Fe₃O₄ and γ-Fe₂O₃ are magnetic. It has been found that the room temperature saturation magnetization and coercivity of the sample after annealing in air at 600°C for 2 hours are much larger than those of the as-deposited films. High resolution TEM characterization confirms that the nanograins are indeed single crystalline. As an example, figure 3 shows a magnetite nanograin of about 15 nm in size. The
measured (111) spacing is 0.49 nm, which is close to the standard value of 0.485 nm (JCPDS 19-0629).

![Figure 2](image2.png)

**Figure 2.** XRD pattern indicate that Fe$_3$O$_4$ (magnetite) and γ−Fe$_2$O$_3$ (maghemite) coexist to form a nanocomposite.

![Figure 3](image3.png)

**Figure 3.** High resolution TEM image of an as-deposited Fe$_3$O$_4$ nanograin.

In the case of MgO as substrates, 0.01M iron (II) acetate was used as the precursor and the deposition was carried out at 400°C for 80 minutes. Figure 4 shows that the nano-islands formed uniformly on the single crystal MgO (100). Our XRD texture characterization (not shown) indicated these nanoislands are epitaxially formed on these substrates, due to the relatively small mismatch between MgO and Fe$_3$O$_4$. The average size of the nanoislands on MgO is smaller than 100 nm, but larger than the previous samples deposited on Si.

![Figure 4](image4.png)

**Figure 4.** (a) FEGSEM image of the Fe$_3$O$_4$ nanoislands formed on MgO (100); (b) AFM image of Fe$_3$O$_4$ nanoislands formed on MgO (100).

![Figure 5](image5.png)

**Figure 5.** Section analysis of the 3-D image of figure 4(b). The result indicates that the room mean square of roughness of sample is less than 2 nm. It means that the Fe$_3$O$_4$ nano-islands on
single crystal were getting more and more flat with increasing time due to possible coalescence. For the section analysis, the height of the highest nano-island in this area is 8.14nm but the average is only 1.478nm. The large average radius value may also indicate the coalescence of the islands.

Figure 5. Section analysis of the AFM image of the Fe₃O₄ nano-islands formed on MgO (100).

4. Conclusions
Nanostructured iron oxides, both Fe₃O₄ and γ–Fe₂O₃ can be successfully deposited onto both single crystal Si (100) and MgO (100) substrates by using ultrasonic spray assisted chemical vapour deposition. XRD and electron microscopy studies reveal that nano-composites of Fe₃O₄ and γ–Fe₂O₃ have been formed on Si with an average size of 20 nm. Moreover, on MgO (100) substrates, epitaxially grown nano-islands have been deposited with a larger size. The result from XRD confirms that in the latter case there is a cube-on-cube epitaxial relationship between Fe₃O₄ nanoislands and the single crystal MgO substrate.

References
[1] Kim W, Kawaguchi K, Koshizaki N, Sohma M, and Matsumoto T, 2003 J. Appl. Phys. 93 8032
[2] Lshikawa M, Tanaka H, and Kawai T, 2005 Appl. Phys. Lett. 86 222504
[3] Zhu JG and Zheng Y, 2000 J. Appl. Phys. 87 6668
[4] Wang KM, Lee DS, Horng L, Chern G, 2004 J. Mag. Magn. Mater. 282 73
[5] Sivakov V, Petersen C, Daniel C, Shen H, Mucklich F, and Mathur S, 2005 Appl. Surf. Sci. 247 513.
[6] Wang J, Chen Q, Zeng C, and Hou B, 2004 Adv. Mater. 16 137
[7] Rager J, Berenov AV, Cohen LF, Branford WR, Bugoslavsky YV, Miyoshi Y, Ardakani M, and J. L. MacManus-Driscoll, 2002 Appl. Phys. Lett. 81 5003
[8] Wei M, Zhi D, and Driscoll JL, 2005 Nanotechnology 16 1364