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Pinning enhancement in MgB_2 superconducting thin films by magnetic nanoparticles of Fe_2O_3

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Abstract. MgB_2 thin films were fabricated on *r*-plane Al_2O_3 ($1\bar{1}02$) substrates. First, deposition of boron was performed by rf magnetron sputtering on Al_2O_3 substrates and followed by a post-deposition annealing at 850 °C in magnesium vapour. In order to investigate the effect of Fe_2O_3 nanoparticles on the structural and magnetic properties of films, MgB_2 films were coated with different concentrations of Fe_2O_3 nanoparticles by spin coating process. The magnetic field dependence of the critical current density J_c was calculated from the M–H loops and magnetic field dependence of the pinning force density, $f_p(b)$, was investigated for the films containing different concentrations of Fe_2O_3 nanoparticles. The critical current densities, J_c, in 3T magnetic field at 5 K were found to be around $2{\cdot}7 \times 10^4$ A/cm^2, $4{\cdot}3 \times 10^4$ A/cm^2, $1{\cdot}3 \times 10^5$ A/cm^2 and $5{\cdot}2 \times 10^4$ A/cm^2 for films with concentrations of 0, 25, 50 and 100% Fe_2O_3, respectively. It was found that the films coated with Fe_2O_3 nanoparticles have significantly enhanced the critical current density. It can be noted that especially the films coated by Fe_2O_3 became stronger in the magnetic field and at higher temperatures. It was believed that coated films indicated the presence of artificial pinning centres created by Fe_2O_3 nanoparticles. The results of AFM indicate that surface roughness of the films significantly decreased with increase in concentration of coating material.

Keywords. MgB_2 thin film; Fe_2O_3 nanoparticles; critical current density; *r*-plane Al_2O_3 substrate.

1. Introduction

The discovery of superconductivity in the compound MgB_2 (Nagamatsu *et al* 2001), with the highest transition temperature, T_c, of 39 K among metallic superconductors, has generated much interest for basic science studies as well as practical applications. MgB_2 is one of the most promising materials because of its simple crystal structure, high critical temperature and relatively long coherence length leading to high critical current density (J_c) due to high transparency at grain boundaries for the current flow (Nagamatsu *et al* 2001; Buzea and Yamashita 2001). For many practical applications of superconductors, the ability to carry high currents in the presence of magnetic fields is very important (Larbalestier *et al* 2001a). Therefore, numerous efforts have been directed towards the improvement of critical current density (J_c), under magnetic fields (Larbalestier *et al* 2001b; Paranthaman *et al* 2001; Xu *et al* 2003; Zeng *et al* 2003; Naito and Ueda 2004). However, J_c of pristine MgB_2 is suppressed rapidly in high magnetic fields due to lack of natural defects (Bugoslavsky *et al* 2001). The high field performance of J_c necessitates introduction of flux pinning centres into MgB_2 grains. For obtaining high J_c, various flux pinning centres are examined in the MgB_2 superconductor.

Magnetism from Fe doping may have a significant effect on the superconductivity of MgB_2. This effect could be more dramatic if the Fe additives are at the nanoscale (Dou *et al* 2005). Several groups reported on the effect of Fe nanoparticles additive on MgB_2 superconductor (Prozorov *et al* 2003; Dou *et al* 2005; Snezhko *et al* 2005). Enhancement of vortex pinning by magnetic Fe_2O_3 nanoparticles embedded into MgB_2 bulk was studied both theoretically and experimentally (Snezhko *et al* 2005). It is possible to increase the pinning strength by producing direct magnetic interaction of vortices with ferromagnetic pinning centres, which was calculated by Snezhko *et al* (2005). It was thought that from these calculations, one can choose an appropriate diameter (about 10 nm) of nanoparticles for the efficient increase of the magnetic pinning force. Prozorov *et al* (2003) studied magnetic Fe_2O_3 nanoparticles embedded in the MgB_2 bulk, resulting in a superconductor–ferromagnetic composite which showed enhancement of magnetic hysteresis due to the magnetic Fe_2O_3 nanoparticles acting as efficient magnetic vortex pinning centres. Dou *et al* (2005) demonstrated that nanoscale Fe particle doping depressed both T_c and $J_c(H)$ in bulk as well as thin film samples (Dou *et al* 2005). In order to elucidate these aspects, it is necessary to investigate the influence of ferromagnetic Fe nanoparticles on MgB_2 thin films.

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This study focused on the effects of magnetic particles coated on the surface of a thin superconducting film. It can explain the origin of pinning centres related to critical current density in the magnetic field. Also, it is believed that the magnetic nanoparticles can improve the physical and mechanical properties. In order to clarify this aspect, we investigated the influence of ferromagnetic Fe_2O_3 nanoparticles coated on MgB_2 thin films. The main goal is to obtain MgB_2 films with high critical current density as well as with the lowest surface roughness.

In this study, the effects of ferromagnetic Fe_2O_3 nanoparticles diffused in MgB_2 thin films grown on r-plane Al_2O_3 $(1\bar{1}02)$ substrates on $J_c(H)$, magnetic field dependence of the pinning force density, $f_p(b)$, T_c and structural properties will be described.

2. Experimental

For this study, MgB_2 thin films were prepared using a two-step synthesis technique and deposited on polished r-plane Al_2O_3 $(1\bar{1}02)$ substrates. MgB_2 films with a thickness of about 600 nm were prepared as described in our previous study (Taylan *et al* 2012). In order to investigate the effect of Fe_2O_3 nanoparticles of 10 nm diameter on the magnetic properties of films, MgB_2 films were coated by a spin coater using 4000 rot/min centrifuge with different concentrations of Fe_2O_3 nanoparticles. Therefore, the entire surface of the films was homogenously coated. Different concentration of the solutions was obtained with the mixture of distilled water and the solution of Fe_2O_3 nanoparticles (Detailed information is given in table 1). In order to dry the coating on the surface of the films, the films were heat treated at 80 °C for 15 min in the furnace.

Table 1. Rate of solution drops of Fe_2O_3 solution and distilled H_2O.

Percentage of solution	Solution drop	H_2O drop
100	1	0
50	1	1
25	1	3

The superconducting transition temperature was determined by magnetic moment–temperature measurement in a magnetic field of 100 Oe, applied perpendicular to the film surface at temperatures between 5 and 50 K using a quantum design physical properties measurement system (PPMS). The magnetic properties (M–H loops) of samples were determined using a vibrating sample magnetometer (VSM) attached to the same system. The magnetization M–H loops of MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles and pure MgB_2 film were measured at H perpendicular to the sample surface for temperature range from 5 to 25 K. Surface roughnesses of the films were characterized using atomic force microscopy (AFM).

3. Results and discussion

Figures 1–3 show change in J_c and magnetization curves of MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles under different magnetic fields applied perpendicular to the film surface at various temperatures ($T = 5$, 15 and 25 K). Critical current density, J_c, was determined from

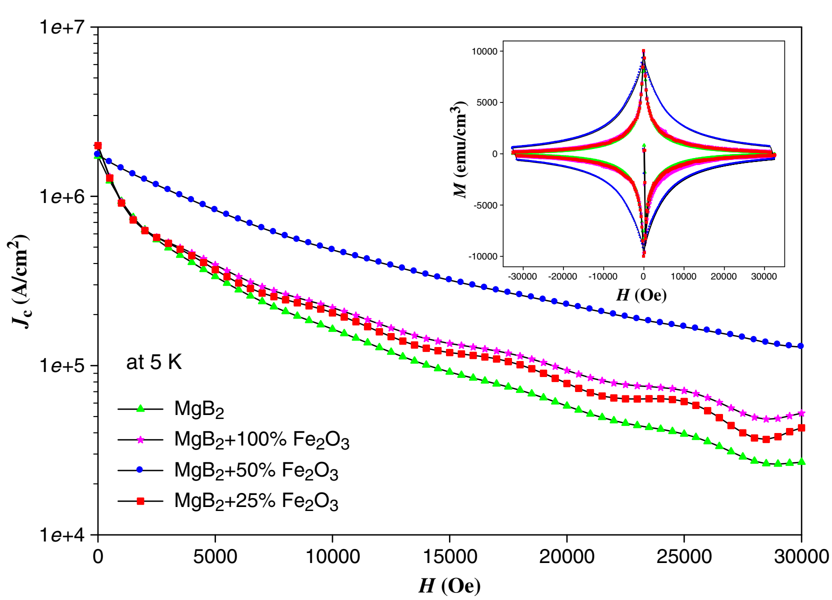

Figure 1. Magnetic field dependence of critical current density (J_c) and magnetization curves (see inset) for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles at 5 K.

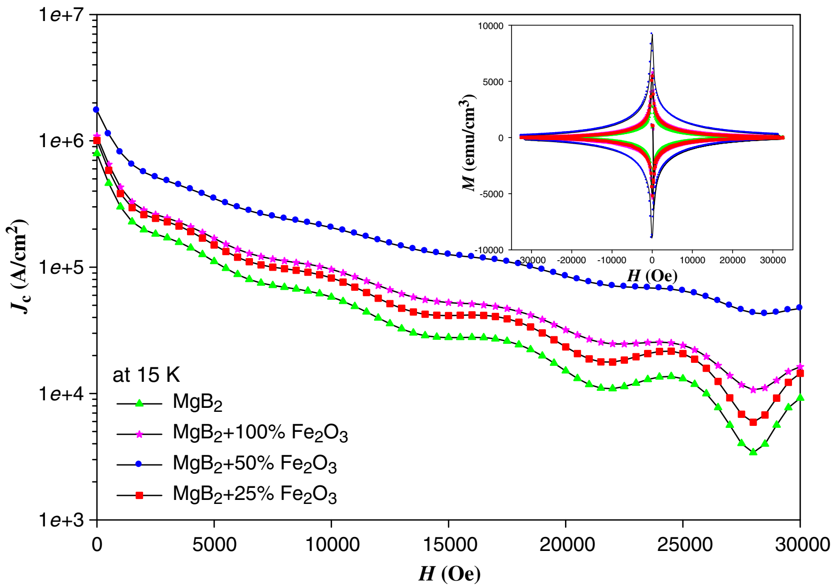

Figure 2. Magnetic field dependence of the critical current density (J_c) and magnetization curves (see inset) for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles at 15 K.

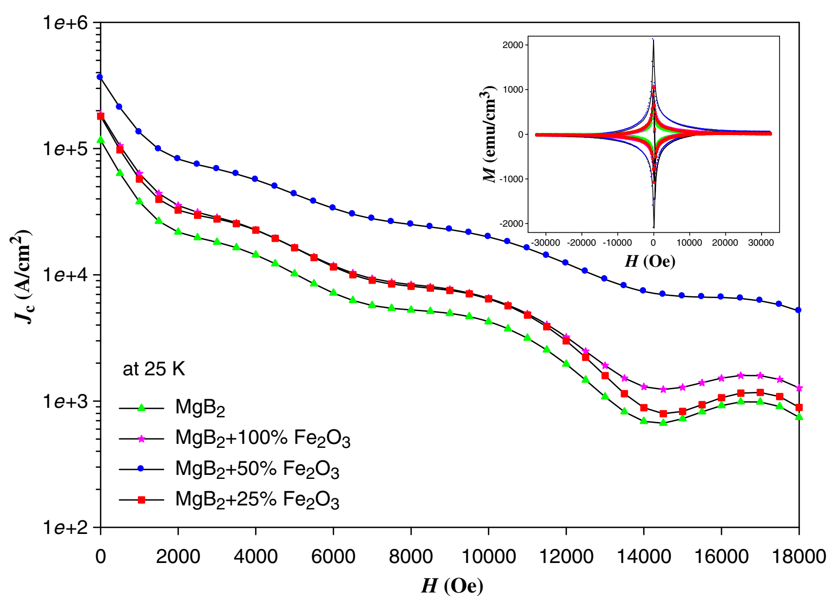

Figure 3. Magnetic field dependence of the critical current density (J_c) and magnetization curves (see inset) for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles at 25 K.

magnetic hysteresis curves. The value of J_c was calculated by using the equation

$$J_c = \frac{20\Delta M}{\left[a(1 - a/3b)\right]},$$

based on Bean's critical state model. In this relationship, ΔM is the difference between the upper and lower branches of the $M(H)$ curve (in emu) divided by the volume of the film (in cm^3): $a \times b$ is the film's surface area, which is perpendicular to the direction of the applied magnetic field with $a < b$ and a and b are in cm, while J_c is in A/cm^2. As seen in figure 1, values of J_c in zero field at 5 K for MgB_2 films uncoated and coated with Fe_2O_3 nanoparticles are approximately the same (2×10^6 A/cm^2). By implementing the magnetic field, values of J_c of MgB_2 films coated with Fe_2O_3

Table 2. Fe_2O_3 concentration and corresponding T_c, J_c for MgB_2 thin films.

Fe_2O_3 concentrations (at.%)	0	25	50	100
T_c (K)	31	29	32	31
J_c (5 K, 0 T) (A/cm^2)	$1{\cdot}7 \times 10^{6}$	2×10^{6}	$1{\cdot}8 \times 10^{6}$	2×10^{6}
J_c (15 K, 0 T) (A/cm^2)	$7{\cdot}9 \times 10^{5}$	1×10^{6}	$1{\cdot}7 \times 10^{6}$	$1{\cdot}1 \times 10^{6}$
J_c (25 K, 0 T) (A/cm^2)	$1{\cdot}2 \times 10^{5}$	$1{\cdot}8 \times 10^{5}$	$3{\cdot}6 \times 10^{5}$	$1{\cdot}9 \times 10^{5}$
J_c (5 K, 3 T) (A/cm^2)	$2{\cdot}7 \times 10^{4}$	$4{\cdot}3 \times 10^{4}$	$1{\cdot}3 \times 10^{5}$	$5{\cdot}2 \times 10^{4}$
J_c (25 K, 1·5 T) (A/cm^2)	$7{\cdot}2 \times 10^{2}$	$8{\cdot}2 \times 10^{2}$	$6{\cdot}8 \times 10^{3}$	$1{\cdot}3 \times 10^{3}$

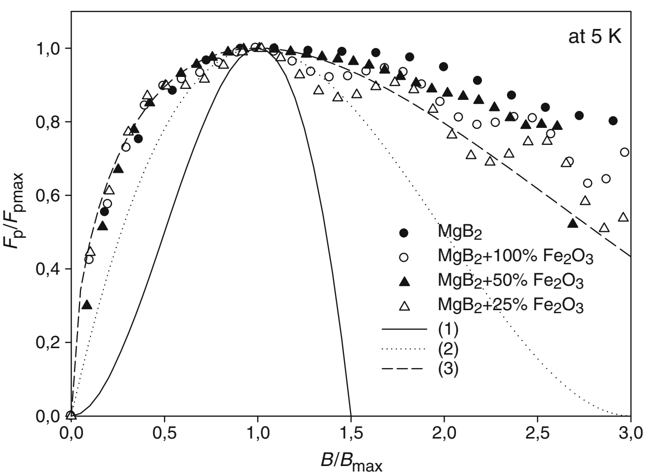

Figure 4. Magnetic field dependence of pinning force density, $f_p(b)$, for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles at 5 K. Solid line represents $\Delta\kappa$ pinning, dotted line, normal point pinning and short dash line, surface pinning.

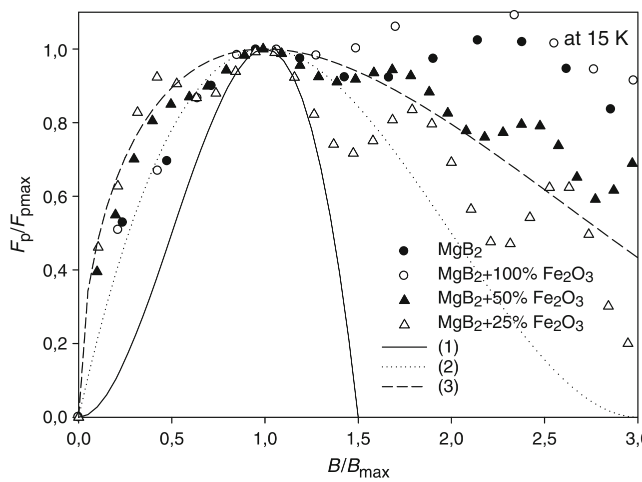

Figure 5. Magnetic field dependence of pinning force density, $f_p(b)$, for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles at 15 K. Solid line represents $\Delta\kappa$ pinning, dotted line, normal point pinning and short dash line, surface pinning.

nanoparticles became higher than that of the uncoated film. Values of J_c in zero fields at 5, 15 and 25 K, in 3 T magnetic field at 5 K, and in 1·5 T magnetic field at 25 K were calculated and listed in table 2. As seen in figure 3 and table 2, the values of J_c in 1·5 T magnetic field at 25 K were calculated to be $7{\cdot}2 \times 10^2$ A/cm^2 for pure MgB_2 film and $6{\cdot}8 \times 10^3$ A/cm^2 for MgB_2 film coated with 50% Fe_2O_3 nanoparticles. The results taken from VSM and the curves of J_c vs magnetic field clearly show that MgB_2 films coated with Fe_2O_3 nanoparticles became stronger against external magnetic field. If one looks at the curves in figures 1, 2 and 3 carefully, changes in J_c with increasing magnetic fields are almost similar to each other and J_c values slightly decrease with the magnetic field. Therefore, it can be said that the flux creep of the films is very low indicating the presence of pinning centres in the films. For these films, the field dependence of J_c is weaker and $J_c(H)$ at higher fields is much higher. It was pointed out that critical current density of the films was slightly decreased in the external magnetic field as a result of influence of artificial pinning centres created by Fe_2O_3 nanoparticles. Our findings are in agreement with the report which claimed that fine Fe_2O_3 particles act as efficient pinning centres to increase $J_c(H)$ (Prozorov *et al* 2003;

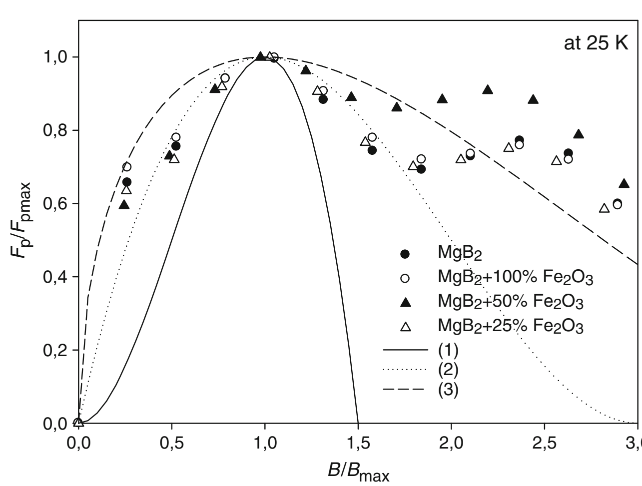

Figure 6. Magnetic field dependence of pinning force density, $f_p(b)$, for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles at 25 K. Solid line represents $\Delta\kappa$ pinning, dotted line, normal point pinning and short dash line, surface pinning.

Snezhko *et al* 2005). However, our findings do not support the report which claimed that doping with Fe nanoparticles had a dramatic depressing effect on $J_c(H)$ (Dou *et al* 2005).

In figures 4, 5 and 6, $f_p = F_p/F_{max}$ vs $b = B/B_{max}$ is plotted for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles for different temperatures. In order to obtain an explicit insight into the pinning mechanism, an extended analysis of $F_p = J_c B$, which represents the pinning force, calculated from figures 1, 2 and 3 was investigated. Normalized pinning force density, $f_p = F_p/F_{max}$ is often scaled with $b = B/B_{max}$, where B_{max} is the field at which the F_p reaches its maximum. The scaling of $f_p - b$ for superconductor samples is often analysed by a few pinning mechanisms, such as

$$\Delta\kappa \text{ pinning}, \quad f(b) = 3b^2\left(1 - \frac{2b}{3}\right), \tag{1}$$

$$\text{Normal point pinning}, \quad f(b) = \frac{9}{4}b\left(1 - \frac{b}{3}\right)^2, \tag{2}$$

$$\text{Surface pinning}, \quad f(b) = \frac{25}{16}\sqrt{b}\left(1 - \frac{b}{5}\right)^2. \tag{3}$$

(Higuchi *et al* 1999; Shigeta *et al* 2003; Shi *et al* 2007).

Equations (1–3) are also presented in figures 4, 5 and 6. f_p is calculated for different concentrations of Fe_2O_3 nanoparticles for different temperatures ranging from 5 to 25 K. As shown in figure 4, below and above B_{max}, all the results for different concentrations of Fe_2O_3 nanoparticles at 5 K scaled in agreement with Eq. (3), indicating that below and above B_{max}, the samples are dominantly affected by the surface pinning. In figures 5 and 6, below and above B_{max}, all the results for different concentrations of Fe_2O_3 nanoparticles at 15 and 25 K are not scaled on a single master curve. In this region of the magnetic field, the plots are located between Eq. (2) and Eq. (3). It may be possible that the uncoated and coated films at 15 and 25 K below and above B_{max} are affected by both surface and normal point pinnings. Eventually, while flux pinning for all the samples is dominated by surface pinning in lower fields and higher fields at 5 K, it is determined to be affected by both the surface and normal point pinnings for all

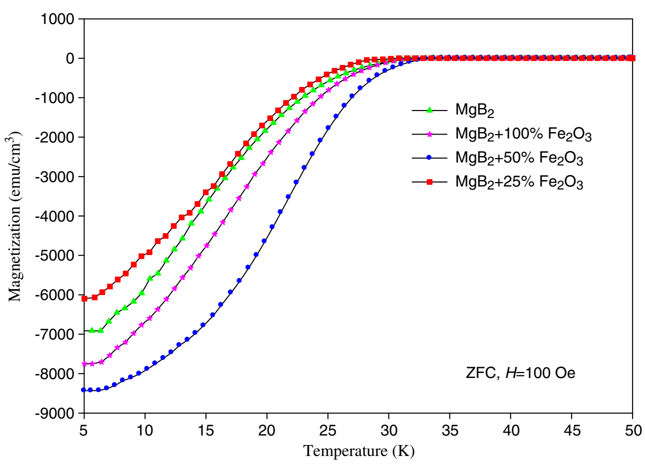

Figure 7. Moment vs temperature curves for MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles. Applied field is 100 Oe for ZFC measurements.

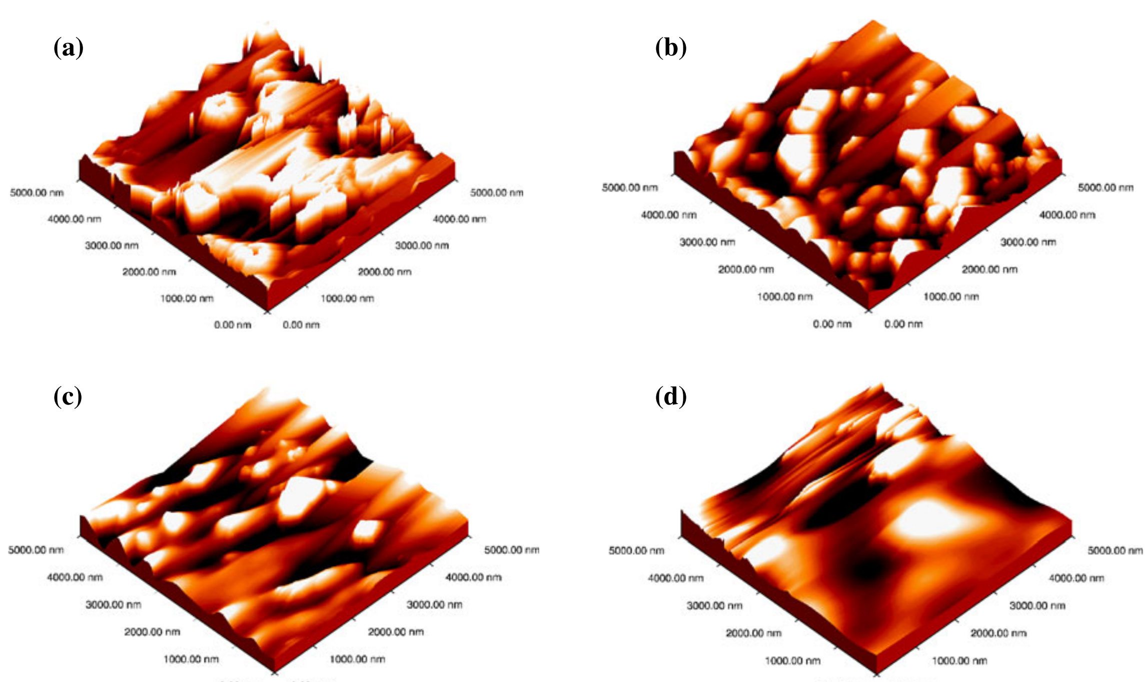

Figure 8. AFM images of MgB_2 films coated with different concentrations of Fe_2O_3 nanoparticles: (**a**) Pristine MgB_2 film, (**b**) MgB_2 film coated 25% Fe_2O_3, (**c**) MgB_2 film coated 50% Fe_2O_3 and (**d**) MgB_2 film coated 100% Fe_2O_3.

the samples in lower and higher fields at 15 and 25 K. Therefore, the scaling on these master curves proved to be difficult. This means that all the samples have different pinning properties at different temperatures (Shigeta *et al* 2003).

The zero field cooled d.c. magnetization curves are shown in figure 7. Superconducting transition temperatures of the films coated with Fe_2O_3 nanoparticles and the uncoated film were determined by measuring the magnetization as a function of temperature. It can be easily understood that the superconducting transition temperature, T_c, varies between 29 and 32 K for MgB_2 thin films. All results of T_c measured by d.c. magnetometer are given in table 2. According to literature, T_c of thin films varies around 30 K which is less than T_c of bulk samples (Yanmaz *et al* 2009). It is well known that T_c depends on the particle size in bulk samples. When one can reduce particle size to nanoscale, T_c will depress to lower temperatures because of stress induced in the particles during the grinding process. In the same interpretation, the thickness of our MgB_2 thin films were determined to be around 600 nm which is much less than commercial powder of MgB_2. Magnetic T_c is lower than the transport T_c for the same set of samples. The difference may arise from the fact that resistivity measurement could be more influenced than magnetization by surface effects (Zhao *et al* 2004).

The 3D AFM images shown in figure 8 were captured with a 5×5 μm scan area of MgB_2 thin films. The images in figure 8(a–d) are for films uncoated and coated with 25, 50, 100% Fe_2O_3 nanoparticles. Root mean square roughness of the films uncoated and coated with 25, 50, 100% Fe_2O_3 nanoparticles was found to be 11·94, 6·27, 2·41 and 1·69 nm, respectively. As clearly seen in figure 8, MgB_2 films become smoother as the concentrations of Fe_2O_3 nanoparticles increase.

4. Conclusions

MgB_2 thin films on *r*-plane Al_2O_3 $(1\bar{1}02)$ substrates have been produced by using a two-step method. In order to achieve expected pinning centres in MgB_2 structure, surfaces of MgB_2 thin films were coated by different concentrations of Fe_2O_3 nanoparticles by spin coating process. Differences between uncoated and coated thin films were clearly distinguished by the critical current density and AFM images. It was clearly observed that MgB_2 films coated with Fe_2O_3 nanoparticles became stronger against external magnetic field and the optimum coating percentage was found to be around 50%. The 3D AFM images clearly demonstrate the correlation between surface morphology and superconducting property.

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