MAGNETORESISTANCE AND ELECTRONIC TRANSPORT OF MAGNETITE NANOCRYSTALS - INDIUM TIN OXIDE NANOCOMPOSITE

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Introduction

For exploration of promising material to realize transparent spintronics devices, intense research has been carried out on room temperature ferromagnetism (RT-FM) of wide band-gap oxides doped with 3d transition metal elements [1-4]. Indium tin oxide (ITO) with RT-FM is especially advantageous for realization of spintronics devices because we have plenty of knowledge and experience about interfaces between ITO and semiconductors/electronic materials. We reported that powders of magnetite nanocrystals (Fe_3O_4 NCs) dispersed in ITO (Fe_3O_4 NCs@ITO composite) prepared in reductive conditions exhibit RT-FM coexisting with superparamagnetism [3]. Highly conducting Fe_3O_4 is well known due to its fully spin-polarized half-metallic band structure and the high Curie temperature of 858 K. By using the Fe_3O_4 NCs@ITO composite powders as a target of pulsed-laser deposition (PLD), we realized RT-FM of PLD-films grown in oxygen partial pressures of 10^{-3} – 10^{-1} Pa [4], and also reported PLD-films grown in oxygen partial pressures lower than 5×10^{-6} Pa exhibiting RT-FM coexisting with superparamagnetism [5]. Here, we report magnetoresistance and electronic transport as well as magnetic properties of the composite powders and thin films.

Experimental

Preparation of Fe_3O_4 NCs@ITO Composite Powders
ITO powders with nominal composition of $In_{1.9}Sn_{0.1}O_3$ were synthesized by a conventional solid-state reaction. The ITO powders were soaked to an ethanol solution of $FeCl_3$ with the concentration of 0.032 mol/L, and then dried and heated at 900 °C for 1h in flowing Ar gas. The molar ratio of In : Fe = 2 : 0.15 was determined by energy dispersive X-ray analysis. The Fe_3O_4 NCs@ITO composite powders demonstrated XRD peaks attributable to the *C*-rare-earth type In_2O_3 cubic cell.

PLD- Fe_3O_4 NCs@ITO Composite Thin Films
For usage as a target of PLD, the Fe_3O_4 NCs@ITO composite powders were pelletized and then sintered at 1500 °C for 1h in flowing oxygen gas. Thin films were grown on the (001) surface of yttria stabilized zirconia (YSZ) substrate at 600 °C in a pressure lower than 5×10^{-6} Pa by using the composite target. An ArF excimer laser with the wavelength of 193 nm was focused onto the target. The repetition rate and energy density were 3 Hz and 1 J/cm^2, respectively. The deposition rate was ≈0.01 nm/cm^2.

Results and Discussion

Fe_3O_4 NCs@ITO Composite Powders
Transmission electron microscopy (TEM) revealed that Fe_3O_4 NCs with diameter of ≈200 nm dispersed in the ITO, as shown in Fig. 1 (a). The particle marked with white dashed line showed the transmission electron diffraction (TED) pattern can be assigned to a cubic Fe_3O_4 crystal lattice with the space group *Fd*3*m*, as shown in the inset of Fig. 1 (a).
The samples demonstrated divergence between the zero-field cooled (ZFC) magnetization and the field-cooled (FC) one, as shown in Fig. 1 (b). Such cooling-history dependence of magnetization is an indication of superparamagnetism.
Figure 1 (c) shows the temperature dependence of R_H/R_0, where R_H and R_0 are resistance measured with

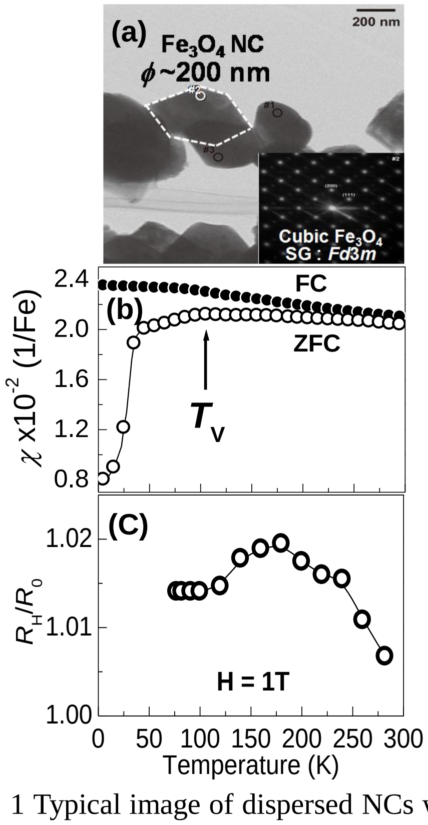

Fig. 1 Typical image of dispersed NCs with diameter of ≈200 nm by scanning TEM (a), the inset of (a) shows TED patterns for the NC marked with white dashed line, temperature dependent *dc* magnetization at *H*=100 Oe (b), and temperature dependence of R_H/R_0 (c) of the Fe_3O_4 NCs@ITO powers.

and without the magnetic field, respectively. The R_H/R_0 value larger than unit indicates positive magnetoresistance for the sample at any temperatures. Such positive magnetoresistance for the composite powders is based on random arrangement of magnetization easy axis of Fe_3O_4 NCs dispersed in ITO matrix since Fe_3O_4 films show negative magnetoresistance ($R_H/R_0 < 1$) at the temperatures [6].

In the temperature dependent resistivity of the composite powders (not shown), the anomaly appeared at ≈110 K corresponding to Verwey transition of Fe_3O_4. We observed Arrhenius type transport behavior with the activation energy of 0.4 meV for the samples in a range of temperature from 110 K to 250 K. This transport property indicates that thermal activated carriers can through large angle grain boundaries between Fe_3O_4 NCs and ITO particles.

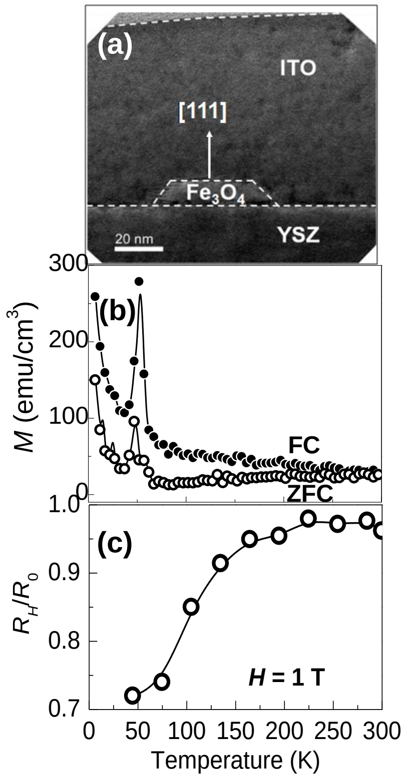

Fig. 2 Typical cross sectional TEM image (a), temperature dependent *dc* magnetization at H=100 Oe (b), and temperature dependence of R_H/R_0 (c) of the Fe_3O_4 NCs@ITO thin films.

Fe_3O_4 NCs@ITO Composite Thin Films

By using TEM, we observed phase–separated Fe_3O_4 NCs with widths of ≈40 nm and heights of ≈10 nm located at the interface between the ITO film and the YSZ substrate, as shown in Fig. 2 (a). High resolution TEM image and selected area electron diffraction patterns revealed that NCs of the cubic Fe_3O_4 are grown epitaxially on the substrate (not shown).

The Fe_3O_4 NCs@ITO thin films exhibited divergence between the FC and ZFC magnetization as shown in Fig. 2 (b). A broad maximum centered around 300 K in the ZFC magnetization, corresponding to blocking of superparamagnetic moments, was also reported for the Fe_3O_4 NCs with diameters of 50 nm [6]. Such magnetic behavior suggests that the composite films are a magnetically diluted system of phase-separated Fe_3O_4 NCs.

Figure 2 (c) shows the temperature dependence of R_H/R_0. The R_H/R_0 values are smaller than unit below 300 K. The Fe_3O_4 NCs@ITO thin films showed negative magnetoresistance. The ratio of MR defined as $100(R_0 - R_H)/R_H$ at 75 K and 165 K amounted to 35 and 5%, respectively. The ratio of MR at 75 K to that at 165 K for the sample (≈7) was rather larger than the one (≈3.3) reported [7]. Such a change in MR is intriguing in relation to the film structure with the Fe_3O_4 and ITO hetero-interface or with the Fe_3O_4 antiphase grain boundary [7].

The transport behavior in Fe_3O_4 bulk is known as a thermal activation type above T_V and a variable range hopping $R = R_0 \exp(a/T)^{1/4}$ type below T_V [7], while the composite film demonstrated the transport character linearly fitted well with $(1/T)^{1/2}$ (not shown) above 45 K. The carrier transport of the film can be explained by a tunneling conductance mechanism [8].

Conclusion

The Fe_3O_4 NCs@ITO powders exhibited positive magnetoresistance attributable to random arrangement of the magnetization easy axis of Fe_3O_4 NCs. On the other hand, epitaxially grown Fe_3O_4 NCs@ITO thin films exhibited negative magnetoresistance due to antiparallel order of the magnetization easy axis of Fe_3O_4 NCs. Electronic transport of the Fe_3O_4 NCs@ITO composite is controlled by the interface between Fe_3O_4 NC and ITO matrix. In the Fe_3O_4 NCs@ITO powders which accompany with large angle grain boundaries between Fe_3O_4 NC and ITO particle, Arrhenius type conduction was dominant in the range of temperature from 110 K to 250 K. In the Fe_3O_4 NCs@ITO thin films including the hetero-interface between Fe_3O_4 NC and ITO film, tunneling conduction was observed above 45 K.

References

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