Nanogranular Co–Al–O films prepared by laser ablation

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Nanogranular Co–Al–O films were prepared by pulsed laser deposition from $\text{Co}_x(\text{Al}_2\text{O}_3)_{1-x}$ targets. Three targets, with different Co volume fractions, were used in order to study the influence of the film composition on magnetic and transport properties. The samples deposited on room temperature substrates exhibit a granular structure consisting of Co grains with the size of few nm embedded in an insulating Al_2O_3 matrix. The magnetic properties show a gradual transition from a low temperature blocked regime to a high temperature superparamagnetic state. It is confirmed by the disappearance of magnetic hysteresis at high temperatures and the temperature dependence of magnetization. Magnetoresistance (MR) higher than 9% at 20 K can be found in $\text{Co}_{26}\text{Al}_{23}\text{O}_{51}$ film.

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1 Introduction Composite materials consisting of metallic grains of nanometer size embedded in an insulating host matrix exhibit special optical, electrical and magnetic properties [1] which offer various technical applications. The study of magnetic nanogranular systems, such as 3-d metal grains in insulating matrix attracts attention due to their fundamental interest (superparamagnetic behaviour) as well as their potential application in sensors, magnetic recording, etc.

Another interesting feature inherent to nanogranular magnetic composites is the tunneling magnetoresistance effect. The conductivity of such materials is provided by tunneling of electrons through an insulating barrier between the grains. Because the tunneling probability depends on the mutual orientation of electron spin and the magnetic moments of particle, the conductivity of material depends on magnetic field. When the moments of the grains are aligned by applied magnetic field the conductivity increases.

2 Experiment Nanocomposite films consisting of Co grains dispersed in an Al_2O_3 matrix were prepared by pulsed laser deposition (PLD) in vacuum of 10^{-4} mbar (see Table 1). A pulsed KrF excimer laser ($\lambda = 248$ nm, $\tau = 20$ ns FWHM, 5–20 Hz repetition rate) was used to ablate targets with an energy density of 3 J/cm^2 , which is above the ablation threshold of the targets. Three different targets, with nominal Co volume fractions of 70.5 (Target 1), 63.5 (Target 2) and 51.3% (Target 3), were prepared by hot press sintering (1400 °C, 30 MPa) of pure Co and Al_2O_3 powder mixtures. The films were deposited at room temperature (RT) or at 400 °C on Si substrates with 200 nm SiO_2 buffer layer.

The magnetizing curves were measured by a physical properties measurement system (Quantum Design PPMS) in the temperature range from 4 to 300 K. The temperature dependence of magnetic moment $m(T)$ after field cooling (FC) and zero-field cooling (ZFC) was investigated by means of SQUID magnetometer (Quantum Design MPMS-5S). The resistance was measured by the four-terminal method using a conventional multimeter. For high resistive samples, an electrometer and the two-terminal method was

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Table 1 Parameters of Co–Al–O films prepared by laser ablation.

sample	target No.	T substrate, °C	pulse number	thickness, nm	chem. comp., at%
mg-1	2	20	20,000	300	Co ₃₈ Al ₂₄ O ₃₈
mg-3	2	400	72,000	240	Co ₅₇ Al ₁₆ O ₂₇
mg-4	1	20	72,000	580	Co ₄₀ Al ₁₅ O ₄₅
mg-5	3	20	72,000	690	Co ₂₆ Al ₂₃ O ₅₁
mg-6	3	400	60,000	200	Co ₄₅ Al ₂₃ O ₃₂
mg-7	1	400	60,000	130	Co ₆₁ Al ₁₆ O ₂₃

used. The chemical composition of films was studied by the electron probe microanalysis on JEOL JXA-733. The thickness of films was measured by a surface profiler (AS 500 Tencor Alphastep).

3 Results

3.1 Chemical composition The chemical compositions of the Co–Al–O films are given in Table 1 and, for better illustration, also shown on the ternary diagram in Fig. 1. The films deposited on heated (open symbols) and room temperature (closed symbols) substrates from the same target (half closed symbol) are denoted by identical symbols. The dashed line corresponds to the stoichiometric composition ratio $\text{Co}_x(\text{Al}_2\text{O}_3)_{1-x}$. As can be seen, the samples produced from the same target differ in the chemical composition. The films deposited on heated substrates are close to the target compositions in contrast to the films deposited at RT, which are Co depleted.

3.2 Magnetization Figure 2a shows the ZFC/FC data obtained on the Co₄₀Al₁₅O₄₅ film. The ZFC/FC bifurcate practically at the temperature T_{max} where the ZFC curve reaches the maximum. For a particle of volume V , blocking temperature (T_B) is defined as the temperature at which the relaxation time, described by the Néel–Brown expression [2], $\tau = \tau_0 \exp(K_a V/k_B T)$, where K_a is the effective uniaxial anisotropy constant of a particle, becomes equal to the measurement time t_m . Assuming $T_B = T_{\text{max}}$ [3] the average diameter of grains, calculated for Co₄₀Al₁₅O₄₅ film, is $d = 5.5$ nm (the magnitude of uniaxial anisotropy constant $K_a = 4.53 \times 10^{-6}$ erg/cc is used [4]). The measurements of other samples show that T_B shifts toward lower temperatures when the concentration of Co decreases. The corresponding d decreases from 6.7 nm (at% Co = 61) to 3.7 nm (at% Co = 26).

Magnetizing curves of the same sample, measured at different temperatures, are shown in Fig. 2b. Above T_{max} a magnetization curve is anhysteretic, as expected in the superparamagnetic state, whereas for $T < T_{\text{max}}$ a hysteresis occurs. The magnetization of the films prepared at RT are not still saturated at field 1.5 T in contrast to the films deposited on heated substrate, where the saturation is achieved at about 0.3 T.

Fig. 1 Chemical composition of Co–Al–O films.

Fig. 2 a) Temperature dependence of ZFC (solid symbol) and FC (open symbol) magnetization for the mg-4 sample. b) Magnetization versus applied magnetic field.

Fig. 3 Electrical resistance vs. temperature of (a) mg-4 sample and (b) mg-7 sample.

Fig. 4 Magnetoresistance curves for film mg-5 measured at (a) 300 K and (b) 20 K.

3.3 Resistivity A typical temperature dependence of resistance for the low Co-concentration film ($\text{Co}_{40}\text{Al}_{15}\text{O}_{45}$) is shown in Fig. 3a. The resistance exhibits a large negative temperature coefficient. The plot of $\log(R)$ versus $T^{-1/2}$ (inset in Fig. 3a) is approximately linear, which is characteristic for tunneling conductivity in insulating nanogranular systems [5]. The resistance of the films deposited on heated substrates (Fig. 3b) is approximately two orders smaller. It increases with decreasing temperature but the temperature dependence is smaller than for the previous sample.

We assume that growth of the films on heated substrates (high Co-concentration films) takes place by the coalescence of the metallic grains so an interconnected network is formed. This can explain their magnetic properties, as well as $R(T)$. The semi-continuous metallic structure (since a percolation path has not been reached yet) is established. Then two mechanisms of conductivity are involved, the metallic conductivity within networks and the electron tunneling through insulating barriers between them.

Fig. 5 Magnetoresistance as a function of at% Co (legend is the same as in Fig. 1).

3.4 Magnetoresistance Figure 4a and b show magnetoresistance curves for $\text{Co}_{26}\text{Al}_{23}\text{O}_{51}$ measured at 300 and 20 K, respectively. A value of MR more than 9% can be observed.

Figure 5 shows the magnitude of MR measured at 77 K as a function of at% Co. A drastic decrease of the MR ratio is found for the films deposited on heated substrates (open symbols). It is probably due to co-existence of two types of conductivity (as it was mentioned above) in these films. The metallic type of conductivity is expected to be less field-dependent that yields the decrease of total MR value.

4 Conclusions The measurements of magnetic and transport properties of the films deposited by laser ablation show that the films prepared on RT substrates consist of single-domain nanosized Co particles embedded in an insulating matrix. The observed blocking temperatures (less than 105 K) correspond to average grain size about 5 nm or less. MR of these films is due to spin dependent tunneling and reaches values higher than 9%. The films deposited on heated substrates show two orders lower resistance and their MR is one order smaller. This can be explained by the appearance of metallic type conductivity in a network of particles that is presumably due to coalescence of the grains.

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