DOI: 10.1017/S143192760550151X
Microsc Microanal 11(Suppl 2), 2005

Crystallographically Orientated fcc Co Nanocrystals in Rutile TiO_2 Thin Film Grown by Pulsed Laser Deposition

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Nanocrystal (NC) assembly has been an important issue in realizing their potentials in nanotechnology. The optical and electronic properties of NC assemblies depend intimately on the orientation of the constituent NCs and their inherent anisotropy. Several experimental methods have been developed to produce oriented nanometer size semiconductors and metallic particles. Here we report the characterization of crystallographically orientated cobalt nano-crystals in rutile thin films by pulsed laser deposition (PLD). This observed phenomena might open up a different route to produce orientated NCs in crystalline materials.

Rutile TiO_2 doped with 7% Co thin films were grown on c-plane Al_2O_3 substrates by PLD from stoichiometric ceramic target $Ti_{0.93}Co_{0.07}O_{2-x}$. The films were grown at 500 ºC at an O_2 pressure of 0.05 mTorr. The film was rapidly cooled down in situ at the same pressure by turning off the heater power supply. The crystalline microstructures were examined in cross section view by a Jeol-2010 transmission electron microscope operated at 200kV. Magnetic properties were measured by a superconducting quantum interference device (SQUID) from 5 to 350K.

At this reduced oxygen pressure during film growth, Co segregated into nanoscale single crystals with sphere-like shape, which dispersed inside rutile TiO_2 film, as illustrated in Fig1a of the TEM cross sectional view. The Co NCs show bright contrast with Moiré fringes that are almost parallel to film/substrate interface. The selected area electron diffraction (Fig.1b) from the film confirms that these individual Co NCs are highly orientated in the film with f.c.c crystal structure. Their (111) planes are parallel to the film surface, with $[11\bar{2}]$Co // [010]rutile and $[\bar{1}10]$Co // [001]rutile. Misfit dislocations between Co NCs and TiO_2 matrix can be identified in the FFT filtered high resolution TEM image (Fig.1c). The extra atomic planes of misfit dislocations at the Co/TiO_2 interface are indicated by lines. The lattice mismatch between Co (111) and rutile (200) is 10.7% with Co having smaller lattice spacing. Therefore the extra planes are in Co NC and their average separation distance is about 9 atomic planes, which indicates a relaxed system. The misfit dislocations are likely to be dislocation loops around the Co particle. The orientation variation of the NCs measured from the diffraction spots is about 5°. From the diffraction pattern, it is seen that the Co NC orientation adopts the host's orientation.

The histogram of the NC size distribution is presented in Fig.2a. Fitting the histogram using a log-normal distribution, yielded a most probable diameter of 4.4 nm with a standard deviation of 0.15 nm. The magnetic properties were measured by SQUID with film surface parallel to the external field. The dc zero-field-cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature (T) is displayed in Fig.2b, which were measured using the standard procedure with a field of 80 Oe. The blocking phenomena characteristic of superparamagnetic nano-particle system is clearly presented in the difference between ZFC and FC curves, and the maximum in ZFC at 105 K is the blocking temperature (T_B) of the Co NC. An estimation of T_B of these sized particles in a non-interacting system can be obtained using the formula $25kT_B = KV$, where k is Boltzman

constant, K is the anisotropy constant, and V, the nanoparticle volume. K increases with decreasing particle size [1]. We take K = 3.02 x 10^5 J/m^3 for a 4nm Co particle [2], and V from the average size measured by TEM (4.4nm). Then T_B should be 33.9 K, considerably lower than the experimental value. There are possibly two contributing factors that give rise to the higher blocking temperature. One is that there is strong dipolar interaction between particles in this system, which has a large effect in pushing T_B higher [3]. The magnetization curve versus T flattens off after the T_B, and the Curie-Weiss temperature T_0 has a large negative value, indicating strong ferromagnetic interaction between Co NCs [3]. The second reason is due to the crystallographic alignment of the Co NCs. It has been reported that aligned NCs have higher blocking temperature [4].

This work was supported by FSU PEG Grant #5024699 and National High Magnetic Field Laboratory under NSF DMR-0084173. DARPA SPINS program with grants HR0011-04-1-0047, MDA972-02-1-0002 and N-00014-99-1-1094 are also acknowledged.

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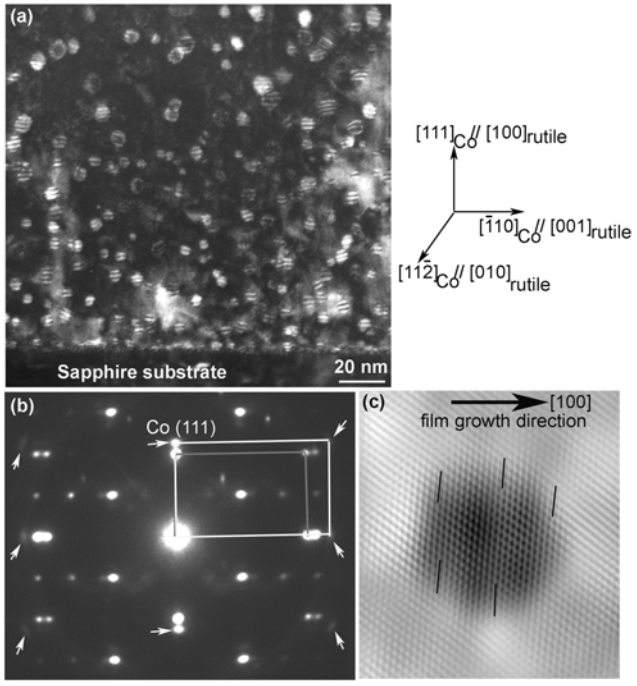

Fig.1 (a)TEM DF image of the cross sectional view. (b)SAD from the film and Co NCs. (c)FFT filtered HRTEM image of one Co NC.

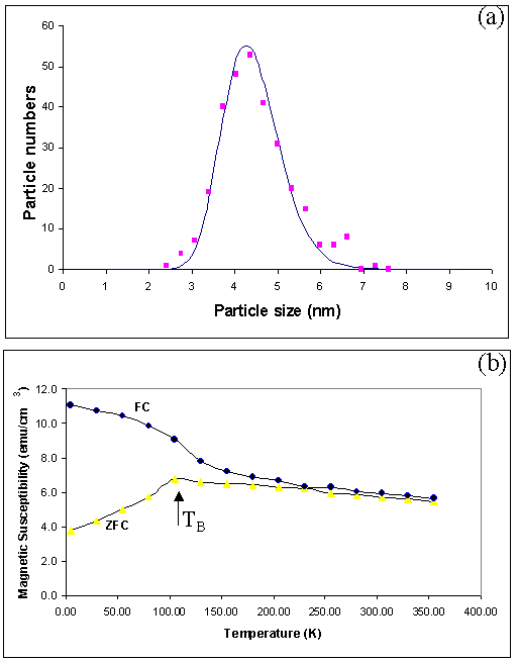

Fig.2 (a)Histogram of Co NC distribution. (b) ZFC and FC magnetization as a function of temperature.

https://doi.org/10.1017/S143192760550151X Published online by Cambridge University Press