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Metallic nanoparticles embedded in an insulator matrix: growth mechanisms, magnetic and transport properties

Z. Konstantinović[1,*], M. García del Muro[1], M. Varela[2], X. Batlle[1] and A. Labarta[1]

[1]*Dpt de Física Fonamental, UB, Martí i Franquès 1, 08028 Barcelona, Spain*
[2]*Dpt de Física Aplicada i Òptica, UB, Martí i Franquès 1, 08028 Barcelona, Spain*

Abstract. Granular thin films constituted of metallic particles (Ag, Co, Au) embedded into a dielectric matrix (ZrO_2) were grown by pulsed laser deposition (PLD) in a wide range of metal volume concentrations x. Transmission electron microscopy (TEM) shows regular distribution of mostly spherical crystalline metal particles with sharp interface with the amorphous matrix. Two mechanisms of particle growth are observed, giving rise to very different values of particle sizes and percolation thresholds. The mean particle size and width of distribution extracted from direct TEM observation and compared to the values obtained by fitting the low field magnetic susceptibility and isothermal magnetization of Co particles in the paramagnetic regime to a distribution of Langevin functions. The dc transport in the dielectric regime is well described in terms of thermally assisted tunneling. The ac transport shows a complex low-frequency absorption phenomenon, directly related with the observed nanostructure.

INTRODUCTION

Granular films constituted of metallic particles embedded into a dielectric matrix [1], comprise a very active research due to their relevant basic properties and potential applications [2]. When particles are reduced to nanometric size their properties are different from those of the bulk state, arising a wide variety of new phenomena, such as finite-size and surface effects, interparticle interactions, and enhanced properties. In order to properly correlate the observed behavior with the corresponding nanostructure and to accurately compare with the theoretical predictions, the experimental model system should contain a narrow size distribution of immiscible nanoparticles very well defined with respect to the matrix. Recent works demonstrate that pulsed laser deposition (PLD) produces granular thin films that are very close to this nanostructured ideal model. In this paper, we concentrate on the structural, transport and magnetic properties of Ag, Co and Au particles embedded in ZrO_2 matrix grown by PLD with the same metal volume concentration x=0.23.

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[*] Present address: *Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus Universitari de Bellaterra, 08193 Bellaterra, Spain,* mail: *zorica@icmab.es*

EXPERIMENTAL DETAILS

Granular Ag-ZrO_2, Au-ZrO_2 and Co-ZrO_2 thin films were grown by KrF pulsed laser deposition (PLD) in a wide range of metal volume concentration [3,4,5,6,7,8,9]. The samples were deposited at room temperature in a vacuum chamber with rotating targets made of sectors of ZrO_2 and pure metal. Different surface ratio of target components led to different metal volume fraction x from metallic to dielectric regime.

Average composition was determined by microprobe analyses. The films are structurally characterized with X-ray diffraction (XRD) and transmission electron microscopy (TEM) [7]. The particle size distribution was also obtained by fitting the low-field magnetic susceptibility (zero-field cooling) and the high-temperature isothermal magnetization curves to a distribution of Langevin functions [5,6,8].

RESULTS AND DISCUSSION

The structural results are compared aiming to stress the effect of the actual microstructure on the percolation threshold. High resolution transmission electron microscopy (TEM) showed regular distribution of spherical Au, Ag and Co nanoparticles having very sharp interfaces with the amorphous matrix (Fig.1)[3,6,7]. The dark regions correspond to the metal particles and light region to the amorphous ZrO_2 matrix. The particles have very well defined interfaces with matrix. Particle size distributions extracted from transmission electron microscopy are well described by log-normal distribution (inset of each TEM picture at Fig.1)[7]. Mean particle size determined from X-ray diffraction agreed with direct TEM observation [7]. It is worth to noting, that for same x and under the same condition of preparation the particle size is strongly dependent on the metal (Au: D_0=2 nm, σ=0.40, Co: D_0=15 nm, σ=0.29 and Ag: D_0=17 nm, σ=0.22).

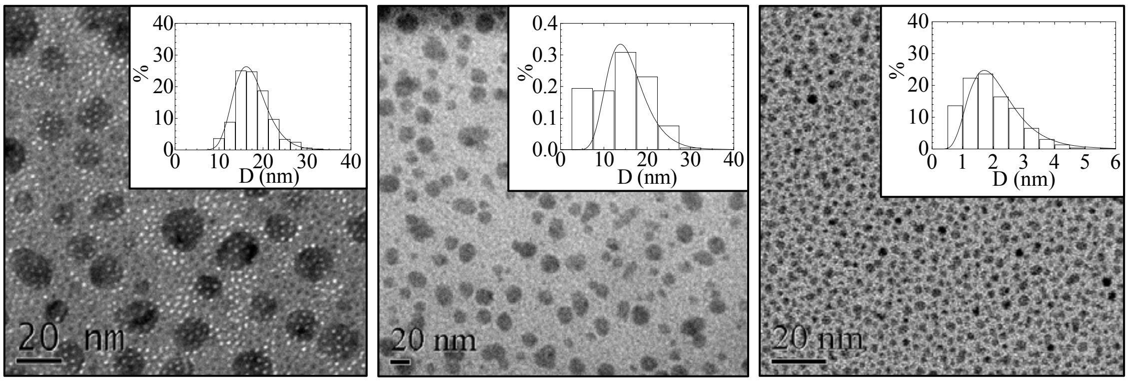

FIGURE 1. From left to right TEM images of Ag-ZrO_2, Co-ZrO_2 and Au-ZrO_2 films with x=0.23. The inset of each figure shows the corresponding particle-size distribution.

Comparing the results for Ag-ZrO_2 and Au-ZrO_2 granular films, two different mechanisms of particle growth as a function of the metal content are evidenced:

nucleation and particle coalescence, their relative significance being different in both granular systems, which yields very different values of the percolation threshold (x_c(Ag)~0.28 and x_c(Au)~0.52)[7]. The values of the average particle size for both silver and gold increase with noble metal concentration, but following very different behaviors. With increasing Au content, mean particle size slightly increases, since in this case, and below about x_{Au}=0.4, particles grow essentially by condensation of the gold atoms available in the neighborhood of each nucleating seed, according to TEM images. However, for Ag-ZrO$_2$, the mean particle size increases abruptly with x_{Ag} because particle growth is arising from nucleation and further coalescence of neighboring particles even at low metal contents.

The Co-ZrO$_2$ system behaves somehow in between Ag and Au, appearing its percolation threshold about x=0.35. Resistivity ρ(T) varies as $\exp(2\sqrt{B/k_B T}$) with B=24.5 meV, indicating thermally assisted tunneling conductance (inset of Fig. 2(a))[1,3,4]. It is worth noting that the ac transport shows a complex low-frequency absorption phenomenon that mimics the universal response of disordered dielectric materials [3,4]. The coexistence of small and big particles (see Fig 1) is required to obtain the observed ac response, allowing both thermally assisted tunneling through small particles and capacitive conductance among larger particles that are further apart [9].

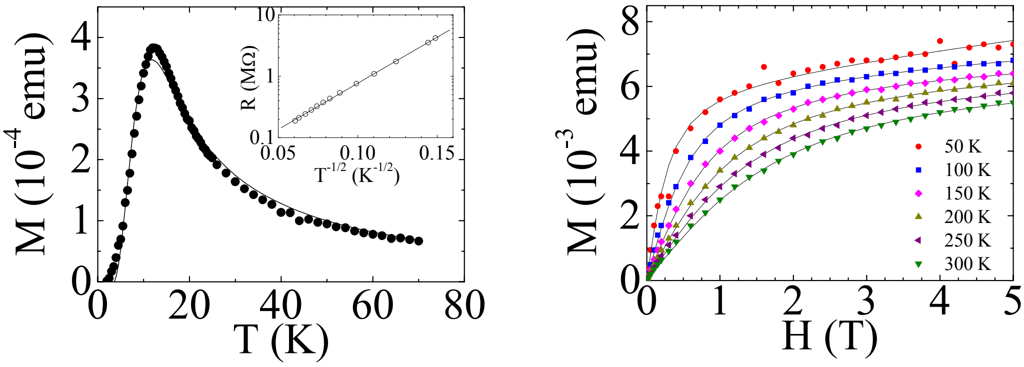

FIGURE 2. (a) ZFC magnetization curve and (b) field dependence of magnetization at different temperatures of Co-ZrO$_2$ for x=0.23. Solid lines are fits to a distribution of Langevin functions (see text). Inset in (a) shows resistivity *vs.* T$^{-1/2}$.

More information about the morphology can be obtained from the magnetic response of Co-ZrO$_2$ (Fig.2). A narrow particle size distribution can be determined by fitting simultaneously the ZFC susceptibility (Fig. 2(a)) and isothermal magnetization curves in the superparamagnetic region (Fig. 2(b)) to a distribution of Langevin functions [5,6,8]. In these calculations the particles are considered to have a log-normal size distribution. The obtained parameters of the particle size distribution are a mean particle size D_0=2 nm and a width of distribution σ=0.12. The average particle size obtained in this way is smaller than that obtained from TEM observation due to strong surface and finite-size effects neglected in these calculations [6].

CONCLUSION

In summary, pulsed laser deposition produces granular thin films with regular distribution of crystalline metal particles with sharp interface with the amorphous matrix. Particle size distributions extracted from transmission electron microscopy are well described by log-normal size distribution. Histograms show very different values of particles sizes depending on the choice of the metal, indicating different particle growth mechanisms and leading to different values of the percolation threshold. The dc transport is governed by thermally assisted tunneling between small close particles. On the other hand, in ac transport, the capacitive conductance between large particles becomes progressively more important as compared to the tunneling contribution, leading to the absorption phenomenon. Mean particle size determined by fitting the low field magnetic susceptibility and isothermal magnetization of Co particles in the paramagnetic regime to a distribution of Langevin functions is underestimated due to neglected surface and finite-size effect.

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