Research Article

Metallic Nanoparticles Embedded in a Dielectric Matrix: Growth Mechanisms and Percolation

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We present a study of the preparation and structural characterization of granular Ag-ZrO₂, Co-ZrO₂, and Au-ZrO₂ thin films grown by pulsed laser deposition (PLD) in a wide range of volume fraction x of metal ($0.08 < x_{\text{Ag}} < 0.28$, $0.06 < x_{\text{Co}} < 0.40$, and $0.08 < x_{\text{Au}} < 0.55$). High-resolution transmission electron microscopy (HRTEM) showed regular distribution of spherical Au, Co, and Ag nanoparticles having very sharp interfaces with the amorphous matrix. The structural results are compared aiming to stress the effect of the actual microstructure on the percolation threshold. Two different mechanisms of particle growing as a function of the metal content are evidenced: nucleation and particle coalescence, with their relative significance depending strongly on the type of metal, giving rise to very different values of the percolation threshold ($x_c(\text{Ag}) \sim 0.28$, $x_c(\text{Co}) \sim 0.35$, and $x_c(\text{Au}) \sim 0.55$).

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1. INTRODUCTION

The latest great advances in fine particle systems field have been promoted by the development of new measuring techniques and refinement of synthesis methods allowing the preparation of particles at the nanometric scale with promising technological applications in many different fields. In particular, granular films, in which a distribution of ultra-fine metallic particles is embedded in a dielectric matrix, comprise a very active research topic. From a fundamental point of view, these composite systems show a variety of behaviors related to percolation processes that the standard percolation theories have not satisfactorily explained yet [1–3]. From technological aspect, spherical particles of noble metals homogeneously dispersed in dielectric matrix exhibit promising optical applications [4–6], associated with its large third-order nonlinear susceptibility [7–9] and ultra-fast response [10] when approaching percolation. When the metal is magnetic, granular magnetic solids are excellent materials to study basic properties, such as finite-size interaction and surface effects, and enhanced and tailored properties [11]. From the technological point of view, their magnetic and magnetotransport properties also suggest attractive

applications, including high coercive films for information storage [12, 13], high-permeability high-resistivity films for shielding and bit writing at high frequencies [14], and giant magnetoresistance for read heads and magnetic sensors [15].

In this paper, we present the preparation and structural characterization by HRTEM of granular Ag-ZrO₂, Co-ZrO₂, and Au-ZrO₂ thin films grown by PLD from a single composite target within a wide range of volume fraction x of metal, from the dielectric regime until percolation ($0.08 < x_{\text{Ag}} < 0.28$, $0.06 < x_{\text{Co}} < 0.40$, and $0.08 < x_{\text{Au}} < 0.55$). Statistical analysis of TEM images provides us with the mean size and width of the size distribution as a function of metal concentration. In particular, we observe that for the three prepared metals, the mean size of the particles increases in a very different way with the metal content. The role played by the two identified growing mechanisms (coalescence and nucleation) is shown to be very different in these three systems, and so leading to different percolation threshold.

2. EXPERIMENTAL

Ag-ZrO₂, Co-ZrO₂, and Au-ZrO₂ granular films were grown by KrF laser ablation (wavelength of 248 nm, pulse duration

FIGURE 1: Bright field TEM images of Ag-ZrO₂ films with (a) $x = 0.08$, (b) $x = 0.18$, (c) $x = 0.23$, (d) $x = 0.26$, and (e) $x = 0.28$. The scale length is indicated in each image. The inset in Figure 1(e) shows lattice fringes inside an Ag particle.

FIGURE 2: Bright field TEM images of Co-ZrO₂ films with (a) $x = 0.06$, (b) $x = 0.12$, (c) $x = 0.25$, (d) $x = 0.30$, and (e) $x = 0.35$. The inset in Figure 2(e) shows lattice fringes inside a Co particle.

FIGURE 3: Bright field TEM images of Au-ZrO₂ films with (a) $x = 0.08$, (b) $x = 0.23$, (c) $x = 0.41$, (d) $x = 0.51$, and (e) $x = 0.55$. The inset in Figure 3(e) shows lattice fringes inside an Au particle.

of $\tau = 34$ ns). The samples were deposited at room temperature in a vacuum chamber with rotating composite targets made of sectors of ZrO₂ and metal (silver, cobalt, or gold). Several surface ratios of target components led to obtaining samples with different volume fractions x of Ag/Co/Au, ranging from metallic to dielectric regimes. The distance between target and substrate was fixed to 35 mm. The laser fluency typically used was about 2 J/cm². Zirconia was stabilized with 7 mol.% Y₂O₃, which provides the matrix with very good properties, such as good oxidation resistance, thermal expansion coefficient matching that of metal alloys, and very high fracture toughness values. It has been observed that ZrO₂ matrix gives rise to sharper interfaces between the amorphous matrix and nanoparticles [16]. Besides, the high oxygen affinity of ZrO₂ prevents oxidation of the metallic nanoparticles.

Sample composition was determined by microprobe analyses. The size distribution of metal nanoparticles was determined from TEM. The substrates for TEM experiments were membrane windows of silicon nitride, which enabled direct observation of as-deposited samples.

3. RESULTS AND DISCUSSION

The analysis of TEM images allowed us to obtain the particles size distribution for each metal concentration. TEM images provide direct observation of the nanoparticles even for very low metal contents. Typical TEM images are shown in Figure 1 for Ag-ZrO₂, in Figure 2 for Co-ZrO₂, and in Figure 3 for Au-ZrO₂. The dark regions correspond to the

Ag, Co, and Au particles and the light regions to the amorphous ZrO₂ matrix. The particles are seen to have clearly defined interfaces with the matrix.

The lattice fringes observed in the metal grains correspond to Ag/Co/Au atomic planes indicating good crystallinity even for very low metal content (see insets to Figures 1–3). Lattice fringes are not present in the ZrO₂ matrix, confirming its amorphous nature.

The particles have spherical shape for $x_{\text{Ag}} < 0.18$, $x_{\text{Co}} < 0.25$, and $x_{\text{Au}} < 0.41$, (see Figures 1(a) and 1(b), 2(a)–2(c), and 3(a) and 3(b)). For $x_{\text{Ag}} > 0.18$, $x_{\text{Co}} > 0.25$, and $x_{\text{Au}} > 0.41$, the neighboring particles start to coalesce, giving rise to larger particles not always with spherical shape (see elongated particles in Figures 1(b)–1(d), 2(d), and 3(c) and 3(d)). Increasing the metal content, the particles form big aggregates (see Figures 1(e), 2(e), and 3(e)), indicating rapid approaching to the percolation threshold, above which metal forms a continuum.

The distributions of particle size are well described by a log-normal function:

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma D} \exp \left[-\frac{\ln^2(D/D_0)}{2\sigma^2} \right], \quad (1)$$

where the fitting parameters D_0 and σ are the most probable particle size and the width of the distribution, respectively, (see Table 1). At low Ag content, the particle size distribution is centered between 1 and 2 nm (see Figure 1(a)). Increasing the Ag content, the size distribution shifts towards larger sizes, due to coalescence of smaller particles into the big ones,

TABLE 1: Particle size distribution parameters obtained from TEM data as a function of the metal volume concentration (x): D_0 (most probable diameter), D_M (average particle diameter, $D_M = D_0 \exp(\sigma^2/2)$), and σ (width of the distribution).

x_{Ag}	D_0 (nm)	D_M	σ
0.08	1.7	1.8	0.40
0.18	11	11.2	0.20
0.23	17	17.4	0.22
0.26	39	39.9	0.21
0.28	220	249.3	0.50
x_{Co}	D_0 (nm)	D_M	σ
0.06	2.0	2.0	0.20
0.12	2.7	2.8	0.25
0.25	7	7.4	0.35
0.30	10.5	11.0	0.30
0.35	14	15.5	0.45
x_{Au}	D_0 (nm)	D_M	σ
0.08	1.2	1.3	0.45
0.23	2	2.2	0.40
0.41	3	3.3	0.45
0.51	5.9	6.1	0.25
0.55	9.5	10	0.32

which produces a net narrowing effect on the particle size distribution (σ goes from 0.4 to 0.2). About $x_{Ag} = 0.28$, the size distribution broadens abruptly ($\sigma = 0.5$) because of massive coalescence of the nanoparticles taking place at percolation.

A quite different evolution of the microstructure is observed for Au-ZrO₂ as the Au content is increased. At low Au content, the width of the particle size distribution is similar to that observed for silver with $x_{Ag} = 0.08$. Nevertheless, in this case, a very smooth shift of the size distribution towards larger sizes is observed even for Au contents as high as $x_{Au} = 0.41$ (see Table 1), suggesting that in a wide range of concentrations Au particles tend to be coated by the matrix, which minimizes particle coalescence and maintains the width of the size distribution almost constant. The onset of coalescence processes takes place about $x_{Au} > 0.41$, giving rise to a similar narrowing of the size distribution (from $\sigma = 0.45$ to $\sigma = 0.25$) as it is also observed in Ag-ZrO₂, but in this case occurring at metal contents very close to percolation. Finally, at $x_{Au} \sim 0.55$ massive coalescence of the nanoparticles arising from percolative processes takes place, which produces a broadening of the size distribution, as it is also observed for Ag-ZrO₂. In the case of the Co-ZrO₂ system, the evolution of the microstructure is closer to Au than to Ag. The coalescence is observed to start about $x_{Co} > 0.25$ (see Figure 2(d)), where the width of the size distribution becomes narrower (see Table 1), and a final increase in σ is observed for $x_{Co} = 0.35$, announcing percolation.

Average particle size for silver, cobalt, and gold increases with metal concentration, but following very different behaviors. With increasing Au content, mean particle size slightly increases, since in this case and below about $x_{Au} = 0.04$,

FIGURE 4: Standard deviation of the size distribution versus metal content.

particles grow essentially by condensation of the gold atoms available in the neighborhood of each nucleating seed, according to TEM images (see Figures 3(a) and 3(b)). However, for Ag-ZrO₂, 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-ZrO₂ is an intermediate case between the extreme behaviors of Au-ZrO₂ and Ag-ZrO₂.

The role played by the two different mechanisms of particle growing observed in Ag-ZrO₂, Co-ZrO₂, and Au-ZrO₂ granular films gives rise to very different values of the percolation threshold in these granular materials. The approach to percolation with the metal content can be better evidenced by the abrupt increase of the standard deviation of the size distribution, defined as $\lambda = D_M[\exp(\sigma^2) - 1]^{1/2}$ [17]. Figure 4 shows the variation of $\lambda(x)$. The metal contents, at which massive particle coalescence preceding percolation takes place, correspond to the range of the $\lambda(x)$ curves where a significant departure from linear behavior is observed. For Ag-ZrO₂, percolation threshold deduced from Figure 4 and according to TEM images ($x_c(Ag) \sim 0.28$) is very close to the theoretical prediction for the model of random percolation of hard spheres [18]. In contrast, particle coalescence in Co-ZrO₂ and Au-ZrO₂ is inhibited by the better efficiency of the matrix to coat the particles with respect to silver ones, which retards the occurrence of percolating processes, shifting the critical value of the metal content to $x_c(Co) \sim 0.35$ and $x_c(Au) \sim 0.55$.

4. CONCLUSIONS

We have shown that pulsed laser deposition is an appropriate technique to prepare silver, cobalt, and gold nanoparticles embedded in ZrO₂ matrix, in a wide range of volume concentration ($0.08 < x_{Ag} < 0.28$, $0.06 < x_{Co} < 0.40$, and $0.08 < x_{Au} < 0.55$). Sharp interfaces between rounded crystalline particles and amorphous matrix are observed in the as-prepared samples, without needing ulterior thermal treatment. The mean nanoparticle diameter increases with metal

volume concentration, but through different mechanisms depending on the metal element. Silver nanoparticles are obtained in a wider range of diameters (1–200 nm) than that corresponding to cobalt (2–15 nm) and gold ones (1–10 nm) which were observed obtained under the same preparation conditions. Distinct microstructures are shown to be the consequence of the relative contribution of the two particle-growing mechanisms: nucleation and particle coalescence. Consequently, the percolation thresholds are very different in these three systems, ($x_c(\text{Ag}) \sim 0.28$, $x_c(\text{Co}) \sim 0.35$, and $x_c(\text{Au}) \sim 0.55$).

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