Particle growth mechanisms in Ag–ZrO$_2$ and Au–ZrO$_2$ granular films obtained by pulsed laser deposition

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Received 12 April 2006, in final form 6 July 2006
Published 28 July 2006
Online at stacks.iop.org/Nano/17/4106

Abstract

Thin films consisting of Ag and Au nanoparticles embedded in amorphous ZrO$_2$ matrix were grown by pulsed laser deposition in a wide range of metal volume concentrations in the dielectric regime (0.08 < $x_{\text{Ag}}$ < 0.28 and 0.08 < $x_{\text{Au}}$ < 0.52). High resolution transmission electron microscopy (TEM) showed regular distribution of spherical Au and Ag nanoparticles having very sharp interfaces with the amorphous matrix. Mean particle size determined from x-ray diffraction agreed with direct TEM observation. The silver mean diameter increases more abruptly with metal volume content than that corresponding to gold particles prepared under the same conditions. Two mechanisms of particle growth are observed: nucleation and particle coalescence, their relative significance being different in both granular systems, which yields very different values of the percolation threshold ($x_{c}(\text{Ag}) \sim 0.28$ and $x_{c}(\text{Au}) \sim 0.52$).

1. Introduction

Granular insulating films, constituted of metallic particles embedded into a dielectric matrix, comprise a very active research field due to their relevant basic properties and potential applications [1]. When particles are reduced to nanometre size their properties are different from those of the bulk state, giving rise to a wide variety of new phenomena, such as finite-size and surface effects, interparticle interactions, and enhanced properties [2, 3]. In particular, from a fundamental point of view, these composite systems show a variety of behaviours related to percolation processes that the standard percolation theories have not satisfactorily explained yet [4–6]. From a technological aspect, spherical particles of noble metals homogeneously dispersed in a dielectric matrix exhibit promising optical applications [7–9], associated with its large third order non-linear susceptibility [10–12] and ultrafast response [13].

In order to correlate properly the observed behaviour with the corresponding microstructure and compare with 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 [14–17] demonstrate that pulsed laser deposition (PLD) produces granular thin films which are closer to this nanostructure model than those films obtained by other techniques, such as sputtering [18–21], sol–gel methods [22, 23] or ion implantation [24, 25]. In particular, granular thin films of composition Co–ZrO$_2$ [14, 17], Ag–Al$_2$O$_3$ and Au–Al$_2$O$_3$ [15, 16] have been previously grown by PLD and studied.

In this paper, we present a complete study of the preparation and structural characterization of granular Ag–ZrO$_2$ and Au–ZrO$_2$ thin films grown by PLD from a single composite target within a wide range of volume fraction $x$ of the noble metal in the dielectric regime (0.08 < $x_{\text{Ag}}$ < 0.28 and 0.08 < $x_{\text{Au}}$ < 0.52). The structural results are compared, aiming to stress the effect of the actual microstructure on the percolation threshold. In particular, we observe that for both noble metals the mean size of the particles increases with the metal content in a similar manner to that reported for samples with an Al$_2$O$_3$ matrix using a two target technique [15, 16].
However, Ag–ZrO₂ and Au–ZrO₂ granular films show two different mechanisms of particle growth as a function of the metal content, which yield very different values of the physical percolation threshold.

2. Experimental details

Ag–ZrO₂ and Au–ZrO₂ granular films were grown by KrF laser ablation (wavelength of 248 nm, pulse duration of τ = 34 ns). The samples were deposited at room temperature in a vacuum chamber with rotating composite targets made of sectors of ZrO₂ and noble metal (silver or gold). Several surface ratios of target components led to obtaining samples with different volume fractions x of Ag/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 cm⁻². 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 the ZrO₂ matrix seems to better coat metallic nanoparticles [14], enabling the occurrence of sharper interfaces between the amorphous matrix and nanoparticles. Besides, the high oxygen affinity of ZrO₂ prevents oxidation of the metallic nanoparticles.

Average sample composition was determined by micro-probe analyses. The size distribution of noble metal nanoparticles was determined from transmission electron microscopy and compared with the average particle size estimated from x-ray diffraction (XRD). The thicknesses of the films prepared for XRD were within 200 and 300 nm. The substrates for TEM experiments were membrane windows of silicon nitride, which enabled direct observation of as deposited samples. Samples prepared for TEM observations were quite thin (in the order of a few nm) and could be considered as a result of almost 2D growth processes. However, this is a necessary condition to achieve visualization of the nanoparticles by this technique. Besides, thin films of a few nanometres in thickness prepared by laser ablation do not grow layer by layer in a continuous manner, but they show inhomogeneous nucleation processes around islands of a hundred nanometres, which yields a quasi-three-dimensional effective growing of the embedded granular structures. Consequently, TEM observations are always two-dimensional images, which indeed can be used to detect the existence of three-dimensional percolative structures in the sample.

3. Results and discussion

Figure 1 shows the x-ray θ–2θ diffraction patterns around the (111) reflection of Ag (a) and Au (b) measured for Ag–ZrO₂ and Au–ZrO₂ films, respectively, for various volume concentrations. The peaks were well defined for high volume content of metal, indicating good crystallinity of the noble nanoparticles.

We should note that, at low volume concentration (x = 0.14 for Ag and x = 0.20 for Au), peaks could no longer be distinguished in a conventional θ–2θ scan, but they were obtained by XRD with grazing beam incidence (ω = 0.30°) in order to maximize the diffraction intensity. For samples with even smaller volume concentrations (x < 0.14) diffraction peaks could not be distinguished even with grazing beam incidence because of too low metal concentration.

From the line broadening it was possible to determine the average particle size by fitting the diffraction peaks to a pseudo-Voigt function.

Table 1. Peak position 2θ, FWHM and average particle diameter Dₐ for several values of x.

| xₐ | 2θₐ (deg) | FWHM (deg) | Dₐ (nm) |
|----|----------|------------|--------|
| 0.28 | 38.22 | 0.54 | 16.2 |
| 0.22 | 38.22 | 1.04 | 8.4 |
| 0.14 | 38.50 | 2.41 | 3.6 |
| xₐ | 2θₐ (deg) | FWHM (deg) | Dₐ (nm) |
|----|----------|------------|--------|
| 0.51 | 38.23 | 1.20 | 7.3 |
| 0.23 | 38.40 | 1.51 | 5.8 |
| 0.20 | 38.40 | 1.81 | 4.9 |

Figure 1. (111) x-ray diffraction for (a) Ag–ZrO₂ and (b) Au–ZrO₂ for different metal contents. Solid lines are fits to a pseudo-Voigt function.
for Ag–ZrO\textsubscript{2} and in figure 3 for Au–ZrO\textsubscript{2}. The dark regions correspond to the Ag and Au particles and the light regions to the amorphous ZrO\textsubscript{2} matrix. The particles are seen to have clearly defined interfaces with the matrix. Moreover, the silver nanoparticles shown by TEM images appear to be significantly bigger and consequently farther apart from each other than gold particles for similar volume concentrations.

The insets in figures 2(b) and 3(b) show a magnification of selected silver and gold particles, respectively. The lattice fringes observed in the metal grains correspond to Ag/Au atomic planes indicating good crystallinity even for very low metal content. Lattice fringes are not present in the ZrO\textsubscript{2} matrix, in agreement with its amorphous nature.

At metal concentration $x_{\text{Ag}} < 0.18$ and $x_{\text{Au}} < 0.41$, the particles have spherical shape (figures 2(a), (b), 3(a) and (b)). For $x_{\text{Ag}} > 0.18$ and $x_{\text{Au}} > 0.41$, the neighbouring particles start to coalesce, giving rise to larger particles not always with spherical shape (see elongated particles in figures 2(b)–(d), 3(c) and (d)). With further increasing of the metal content, $x_{\text{Ag}} \geq 0.28$ and $x_{\text{Au}} \geq 0.52$, the particles form big aggregates (figures 2(e) and 3(e); note the different scale length in comparison with the rest of the TEM images), indicating a rapid approach to the percolation threshold, above which the metal forms a continuum.

TEM micrographs were analysed in order to quantify the particle size distributions shown in figures 4 and 5 for Ag–ZrO\textsubscript{2} and Au–ZrO\textsubscript{2}, respectively. The distributions of particle size are well described by a log-normal function:

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

where the fitting parameters $D_0$ and $\sigma$ are the most probable particle size and the width of the distribution, respectively (see table 2). At low Ag content, the particle size distribution is centred between 1 and 2 nm (figures 4(a) and 4(a)). Increasing the Ag content, the size distribution shifts to larger sizes, due to coalescence of smaller particles into the big ones (figures 4(b)–(d)), which produces a net narrowing effect on the particle size distribution. About $x_{\text{Ag}} = 0.28$ (figure 4(e)) the size distribution broadens abruptly because of massive coalescence of the nanoparticles taking place at percolation. However, a quite different evolution of the microstructure is observed for Au–ZrO\textsubscript{2} as the Au content is increased. At low Au content, the width of the particle size distribution is similar.
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Figure 4. Distribution of particle sizes as a percentage, obtained after analysis of the TEM micrographs for Ag–ZrO$_2$ with (a) $x = 0.08$, (b) $x = 0.18$, (c) $x = 0.23$, (d) $x = 0.26$ and (e) $x = 0.28$. The solid lines are fits to a log-normal distribution.

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 $x_{Au} = 0.41$ (figures 5(a)–(c)), 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 $x_{Au} > 0.41$ (figure 5(d)), giving rise to a similar narrowing of the size distribution as also observed in Ag–ZrO$_2$, but in this case occurring at metal contents very close to percolation. Finally, at $x_{Au} \sim 0.52$ massive coalescence of the nanoparticles arising from percolative processes takes place, which produces a broadening of the size distribution (figures 3(e) and 5(e)), as also observed for Ag–ZrO$_2$.

The dependence on the metal volume concentration of the average particle sizes $D_M$ for silver and gold, obtained from log-normal distributions (open symbols) and the broadening of (111) metal reflection (solid symbols), are in good agreement, as shown in figure 6. The values of the average particle size for both silver (triangles) and gold (circles) increase with noble metal concentration, but following very different behaviours. With increasing Au content, mean particle size slightly increases (figure 5(b)), since in this case and below about $x_{Au} = 0.4$ particles grow essentially by condensation of the gold atoms available in the neighbourhood of each nucleating seed (figures 5(a) and (b)), according to TEM images (figures 3(a) and (b)). 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 neighbouring particles even at low metal contents.

The two mechanisms of particle growth observed in Ag–ZrO$_2$ and Au–ZrO$_2$ granular films give rise to very different
Figure 3(e). In contrast, spherical nanoparticles in Ag–ZrO₂ have sharp interfaces with the matrix. The mean nanoparticle diameter increases with metal volume concentration. Silver nanoparticles are obtained in a wider range of diameters (1–200 nm) than that corresponding to gold ones (1–10 nm) obtained under the same preparation conditions. Besides, Ag–ZrO₂ and Au–ZrO₂ granular films show very different microstructures, as a consequence of the relative contribution of the two particle growth mechanisms: nucleation and particle coalescence. Consequently, the percolation thresholds are very different in these two systems (x̄c(Ag) ∼ 0.28 and x̄c(Au) ∼ 0.52).

### Acknowledgments

We would like to thank the staff of the scientific and technical facilities of UB. Financial support of the Spanish CICyT (MAT2003-01124) and the Catalan DURSI (2005SGR00969) are gratefully recognized. ZK thanks the Spanish MEC for the financial support through the Juan de la Cierva programme.

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### Values of the Percolation Threshold

Values of the percolation threshold for Ag–ZrO₂, the percolation threshold deduced from TEM images (x̄c(Ag) ∼ 0.28) is very close to the theoretical prediction for the model of random percolation of hard spheres [26]. In contrast, particle coalescence in Au–ZrO₂ is inhibited by the better efficiency of the matrix to coat gold particles with respect to silver ones, which retards the occurrence of percolating processes, shifting the critical value of the metal content to x̄c(Au) ∼ 0.52 (see figure 3(e)).

The diameters of gold nanoparticles for Au–ZrO₂ are similar to those reported for Au–Al₂O₃ granular films for similar metal contents [2, 16], suggesting that the nature of the matrix does not play a crucial role in this case, provided it is amorphous. In contrast, spherical nanoparticles in Ag–ZrO₂ are observed in a wider range of diameters (within 2 and 17 nm) than that corresponding to Ag–Al₂O₃ (within 1 and 3 nm) [15].

### Percolation Threshold

Percolation threshold is determined as the highest metal content just below the point where formation of percolative structures between the particles is evidenced from TEM images, which occurs when massive coalescence processes dominate particle growth (this can be also detected by an abrupt broadening of the size distribution). Preliminary results from transport measurements show that the percolation threshold takes place at slightly smaller values than those deduced from the analyses of TEM images, which is related to the formation of three-dimensional conduction paths.

### Table 2

| x̄c(Ag) | D̄₀ (nm) | D̄ₐ (nm) | σ |
|--------|----------|---------|---|
| 0.28   | 220      | 249     | 0.50 |
| 0.26   | 39       | 40      | 0.21 |
| 0.23   | 17.0     | 17.4    | 0.22 |
| 0.18   | 11.0     | 11.2    | 0.20 |
| 0.08   | 1.7      | 1.8     | 0.40 |

| x̄c(Au) | D̄₀ (nm) | D̄ₐ (nm) | σ |
|--------|---------|---------|---|
| 0.52   | 9.5     | 10.0    | 0.32 |
| 0.50   | 5.9     | 6.1     | 0.25 |
| 0.41   | 3.0     | 3.3     | 0.45 |
| 0.23   | 2.0     | 2.2     | 0.40 |
| 0.08   | 1.2     | 1.3     | 0.45 |

### 4. Conclusions

We have demonstrated that pulsed laser deposition is an appropriate technique to prepare silver and gold nanoparticles embedded in ZrO₂ matrix, in a wide range of volume concentration (0.08 < x̄c(Ag) < 0.28 and 0.08 < x̄c(Au) < 0.52). As prepared films without ulterior thermal treatment show rounded particles of noble metal, which are crystalline and have sharp interfaces with the matrix. The mean nanoparticle diameter increases with metal volume concentration. Silver nanoparticles are obtained in a wider range of diameters (1–200 nm) than that corresponding to gold ones (1–10 nm) observed under the same preparation conditions. Besides, Ag–ZrO₂ and Au–ZrO₂ granular films show very different microstructures, as a consequence of the relative contribution of the two particle growth mechanisms: nucleation and particle coalescence. Consequently, the percolation thresholds are very different in these two systems (x̄c(Ag) ∼ 0.28 and x̄c(Au) ∼ 0.52).
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