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Thermal morphological evolution of platinum nano-particles in Pt–Al_2O_3 nano-composites

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Abstract

Temperature morphological evolution of nonpercolated granular nano-structures of platinum nano-particles embedded in an insulating alumina matrix was investigated by X-rays scattering in grazing angle reflection mode. In the investigated temperature range of 298–823 K, it was found that the annealing treatment tends to increase the Pt nano-particles' size and to produce a quasi-mono-disperse Pt nano-particles followed by a reduction of the barrier thickness between them. The percolation temperature is estimated to be of the order of 890 K. Using the rate constant governing the growth of the Pt nano-particles, the corresponding activation energy was determined to be about 90 kJ/mol.

Keywords: Nano-composites; Percolation process; Growth process; Small angle X-ray scattering; Grazing incidence

1. Introduction

Granular nano-composites, also called nano-phased structures exhibit an interesting state of matter intermediate between the bulk crystalline state and the nano-crystalline, generally amorphous state. Far from the percolation threshold, they consist of isolated metallic nano-particles implanted in a host insulating matrix. The granular nano-structures have long been interesting subject owing to their desirable optical, magnetic, superconducting or electric properties for on the one hand, and to their physical fundamental behavior in an other hand [1–5]. Recently, it was established experimentally the possibility of observing small angle X-rays scattering in a grazing angle reflection geometry in such a type of thin films containing

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metallic inhomogeneities [6,7] where the embedded nano-particles' characteristics were deduced. The current short communication which is complementary to the previous theoretical and experimental work [7], is devoted to the investigation of thermal kinetic evolution of the platinum nano-particles in the Al_2O_3 hosting matrix. More accurately, the Pt average diameter $\langle\phi\rangle$, average inter-platinum distance $\langle\xi\rangle$ and their corresponding distributions σ_ϕ and σ_ξ are investigated versus the heating temperature. Moreover, the percolation temperature T_P, a temperature for which the Pt nano-particles start to touch each other is estimated.

To shed-light on the above questions, we have investigated the thermal effect in a low temperature range of 298–823 K of a granular Pt_X–Al_2O_3 nano-composite close to the percolation threshold so to promote a percolation process if any. The platinum nano-particles volume concentration has been selected sufficiently almost near the percolation value. Three main rationales justify the present contribution which lies with the scope of the previous study [7]. Firstly, understanding how the Pt nano-particles' morphology changes with temperature would be advantageous in tailoring the physical properties for a given application. Secondly, it seems that there is no exhaustive experimental results within the literature in the considered temperature range except some works achieved by transport measurements or transmission electron microscopy [8,9]. But as underlined in the previous paper [7], the investigation by X-rays scattering in the considered grazing angle reflection mode [10,11] is more accurate regarding the statistical precision on the determination of the nano-composite's characteristics: 10^{12} and 10^3 investigated particles for the X-rays and transmission electron microscopy respectively while the electrical measurements do not provide a direct experimental evidence of the Pt nano-particles' morphological characteristics. Thirdly, a recent work shows that a new phase Al_2O, corresponding to a minimum free energy can be formed and even stabilized at the Pt nano-particle/Al_2O_3 matrix interface [12].

2. Experimental results and discussion

A nonpercolated granular Pt–Al_2O_3 nano-structure of approximately 1003 nm in thickness is considered. It is grown by RF sputtering in an inert-gas atmosphere of pure argon and deposited on a cleaned cooled float-glass substrate. The volume concentration of the Pt nano-particles "X" is about 38%, just slightly below the percolation concentration. Isochrone heat treatments of the sample were carried out in high vacuum "pressure before heating $\approx 10^{-8}$ Torr" in an electric furnace with a heating rate of 5 K/min. The sample was inserted in the furnace when the desired temperature is reached and was extracted 3 hours after. The annealing temperatures were 298, 523, 623, 723 and 823 K. The maximal annealing temperature was imposed by the softening temperature of the float-glass substrate which is approximately 990 K. The X-rays reflectivity measurements were conducted on a Θ–2Θ reflectometery unit with a $Cu_{K\alpha}$ radiation 1.5405 Å, covering an extensive range of momentum $Q_Z = 4\pi \sin\Theta/\lambda$, $0.2 \leqslant Q_Z \leqslant 4.0\ \text{nm}^{-1}$.

The transmission electron microscopy studies of the nonannealed sample illustrated quasi-spherical isolated platinum nano-particles of about 4 nm in average diameter well dispersed in the Al_2O_3 matrix 13. The X-rays diffraction measurements indicate that Pt nano-particles are polycrystalline while Al_2O_3 host matrix is amorphous. Fig. 1 reports the X-rays reflectivity profiles in a logarithmic scale versus the scattering vector Q_Z for the 4 investigated heated samples in addition to the nonheated reference sample. At small Q_Z values, the incoming X-rays beam is totally reflected giving rise to the plateau of total reflection in each case. Over this region, usual Kiessig interference fringes, due to the finite total thickness of the Pt–Al_2O_3 granular nano-structures, are observed. As well established, this interference set characterizes the continuous aspect of the nano-structures [7]. However, to simulate the reflectivity profiles, the considered model of Fig. 2 was the most adequate. It consists of a granular layer 2 sandwiched between two thin layers located at the substrate layer 1 and air layer 3 interfaces respectively. This model which was initially considered and treated theoretically by Rauscher et al. [6] seems more realistic because the annealing should induce an interfacial diffusion at the nano-structure/substrate interface and a possibly a contamination at the nano-structure/air interface. The simulation of both total reflection plateau and the Kiessig fringes set allows to deduce the mean electron density, thickness and interfacial roughness of each of the 3 layers of Fig. 2.