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Ultra thin films of gadolinium deposited by evaporation in ultra high vacuum conditions: Composition, growth and morphology

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ABSTRACT

Ultra-thin gadolinium films with thicknesses between 8 and 101 Å were deposited on AT-cut crystalline quartz substrates under ultra high vacuum conditions, and subsequently subjected to composition and morphologic characterization through X-ray photo-spectroscopy analysis and atomic force microscopy. Oxygen contamination is found on the samples, and its amount is estimated in terms of the thickness of an oxygen layer over the gadolinium films after subtracting the contribution to the XPS spectra of the underlying background. Atomic force microscope pictures provide evidence of having metal island films, with two growing regimes: the Volmer–Weber mode for the thinner films considered and the Stranski–Krastanov growing mode for the thicker ones. From evaluation of the sticking coefficient, the shape of the islands is approximated in terms of oblate spheroid caps and variation of the contact angle with film mass thickness is reported.

1. Introduction

Behind many applications developed until today, or potentially available to be developed, physical properties of small metal particles have been a subject of interest since a long time ago, being the optical properties of composites (metal particles randomly distributed through a dielectric matrix) one of the first topics deeply considered due to applications as selective solar-absorbing surface coatings [1]. The interaction between noble metal nanoparticles and electromagnetic radiation opens the possibility of having highly intense and localized electric fields, which has promote the development of surface enhanced Raman scattering based techniques for the chemical analysis of adsorbed molecules and proteins [2]. The excitation of surface plasmons in noble metal nano-particles in aqueous solutions allows the study of electrochemical processes happening in the metal–water interface [3]. The bactericidal effect of nano-sized metal particles is other research issue currently developed for interdisciplinary groups [4]. Another area of interest involves what is called metal hydride systems. The optical properties of metal hydride systems are of great interest owing to technological implications involved in this topic, for example gas sensors, electrochromic materials, and switchable mirrors. The first generation of these metal hydrogen systems consisted of hydrided rare-earths in which the systems change from reflecting to semitransparent states maintaining some coloration when approaching the semiconductor trihydrides [5]. In order to improve color neutrality, a second generation was developed consisting of hydrided magnesium alloyed with some rare-earths to improve the hydrogenation–dehydrogenation cycles [6]. The presence of some rare-earth metals in these hydride systems favors oxidation and degradation limiting the development of technological applications. In order to avoid this as much as possible a third generation was developed based on magnesium-transition metal alloys [7]. Nowadays a fourth generation of metal hydride systems is emerging. Similar materials are being considered but now the presence of an experimentally tailored nanostructure, and its effect on optical and electronic properties, is the main subject to be analyzed. Gadolinium hydride is one of the systems previously considered in our research group when studying the evolution of its optical properties with hydrogen absorption by quasi-homogeneous Gd:H thin films whose thicknesses are about 500 Å [8]. In this work non-homogeneous Gd ultra-thin films are considered. From a basic point of view, the interaction between metal particles and electromagnetic radiation is very sensitive to the size and shape of the particles. This issue will become very significant when considering optical properties of Gd and Gd:H ultra thin films. Sometimes the average shape of the particles is described in terms of spheres or spheroids just for simplicity or due to the lack of a precise characterization of the particle shapes.

In this paper we report on the growth, composition and morphology of gadolinium ultra-thin films with thicknesses between 8 and 101 Å, deposited on crystalline quartz substrates at room temperature. The analysis reported here will be valuable in the

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near future when considering hydrogenation of ultra thin Gd films. These films have a metal island structure whose average size and morphology of the metal particles are determined from atomic force microscope (AFM) pictures. Section 2 contains a brief description of the sample deposition under ultra high vacuum (UHV) conditions. Section 3 focuses on the analysis of the chemical composition based on X-ray photospectroscopy (XPS) measurements, as well as on quantification of an observed oxygen contamination. Growth and changes in morphology of the films with increasing mass thickness is the subject of Section 4, where we show how the analysis of the AFM pictures provides evidence of a transition from the Volmer–Weber to the Stranski–Krastanov growing modes. Changes of the sticking coefficient and the contact angle with increasing mass thickness of the films are reported. Our main achievement has been the development of a procedure to characterize, with more detail, the average size and shape of metal islands on dielectric substrates from data provided by AFM pictures and physical parameters related to the deposition setup.

2. Sample preparation and measurements

Several samples were obtained with thickness ranging from 8 to 101 Å. Samples were prepared in an UHV system using a home-made electron beam evaporation source [9]. Gd (99.9% pure) is held in a small W basket and kept under an electric potential between 1.5 and 2.0 kV, 4 mm close to a W filament. Evaporation conditions are reached by investing less than 160 W of power. Out-gassing is prevented by keeping the evaporation source surrounded by a liquid nitrogen shroud. Base pressure was $(7 \pm 3) \times 10^{-11}$ mbar. During evaporation, pressure increases with time. For the thickest samples pressure reached 3.5×10^{-8} mbar. The average evaporation rate, measured next to the substrate, was 0.2 Å/s. Samples were grown at room temperature, $T = (295 \pm 3)$ K, on AT-cut quartz substrates pre-cleaned with acetic acid, de-ionized water, anhydride alcohol, acetone and heated at 450 K for a period of 3 h in the vacuum system prior to deposition.

Film mass thickness and evaporation rate were measured in situ with a gauged quartz microbalance, QCM (Maxtek Inc., model TM-200), with a measured uncertainty in the film mass of 2%. Samples were studied in situ at pressures in the upper 10^{-11} mbar range to ensure clean surfaces. Chemical analysis of the samples is carried out by X-ray photoelectron spectroscopy (XPS) performed after deposition. XPS spectra of ultra-thin films were measured in situ with a Staib Instruments Cylindrical Mirror Analyzer Spectrometer using a PSP Vacuum Technology source of Al K_α X-rays at a characteristic energy of 1486.6 eV. Data taken on consecutive days using the same sample showed no appreciable variation which indicates a good adhesiveness and stability of the films.

3. Composition analysis: XPS quantification in Gd samples

The XPS spectra were first corrected for the energy dependence of the analyzer transmission function. Then a straight line was fitted in a small energy region on the high energy side of the peak and subtracted from the entire spectrum. Fig. 1 shows the obtained spectrum with Al K_α X-rays after physical evaporation of a gadolinium thin film 101 Å thick on a crystalline thick quartz substrate. The binding energy peaks corresponding to $3d_{3/2}$ and $3d_{5/2}$ excited electrons are clearly displayed, with values of 1220.0 and 1188.0 eV respectively relative to the Fermi level. The corresponding values reported in the literature are 1221.9 and 1189.6 eV [10]. Some oxygen contamination, whose amount will be determined in terms of an effective oxygen surface layer covering the metal island films, is also found, as well as a peak due to Gd MNN transitions. No evidence of contamination from the tungsten basket or filament was found from this XPS analysis.

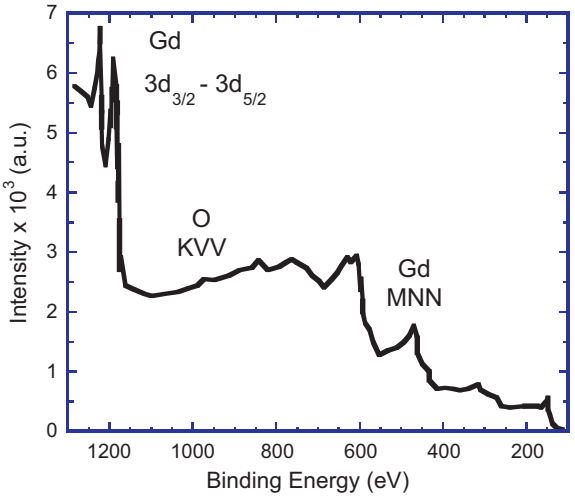

Fig. 1. XPS survey scan of a 101 Å thick Gd sample carried out immediately after physical evaporation. The doublet peak of the metallic Gd is in concordance with values reported in the literature [10].

Qualitative elemental identification is usually achieved by comparing the peak binding energies with tabulated values. On the other hand, quantitative analysis means relating photoelectron peak intensities to surface composition. However, determination of the peak area is influenced by the peak shape and the underlying background, the atomic sensitivity factor and the inelastic mean free paths of the electrons [11–13]. In agreement with Seah and Dench [14], for ultra-thin films with contamination over its surface, the signal of the substrate B covered by a thin layer A of thickness D is given as follows:

$$\frac{I_B}{I_A} = \frac{S_B(1 - \exp(-D/\lambda_B))}{S_A \exp(-D/\lambda_A)} \quad (1)$$

with S_A and S_B as the corresponding atomic factors, and where λ_A and λ_B are the inelastic mean free path of the electrons through both media respectively. Our calculations used the atomic factors defined by Wagner et al. [13], and Seah and Briggs approximation for the inelastic mean free paths of the electrons [12], i.e., $\lambda_n = A_n/E^2 + B_n\sqrt{E}$ with $n = A$ or B, A_n and B_n as fitting parameters, and E as the kinetic energy of the electrons above the Fermi level, in eV. A number of background subtraction approaches for quantification in XPS analysis have been proposed in the literature [14,15]. One of the most widely used is the method of Shirley [16], who assumes a constant (energy-independent) probability for energy losses. This leads to a simple and iteratively calculated subtraction method in which the background intensity at a given energy is directly proportional to the intrinsic peak area at the high kinetic energy side. According to Shirley, the background is subtracted iteratively from the measured spectrum $j(E)$ as:

$$F_{k+1}(E) = j(E) - j(E_{\min}) \frac{\int_E^{E_{\max}} F_k(T)\mathrm{d}T}{\int_{E_{\min}}^{E_{\max}} F_k(T)\mathrm{d}T} \quad (2)$$

where $F_k(T)$ is the background corrected spectrum after k iterations. The series converges typically after a few iterations and as mentioned the background is directly proportional to the peak area at the high kinetic energy side. For Shirley's background, the only parameters needed are the end points of the range over which the subtraction is carried out, i.e., $E_{\min}$ and $E_{\max}$. The starting point in Fig. 2 was set at the high binding energy side of the $3d_{3/2}$ peak, i.e., 1245 eV, and the end point to the local intensity minimum at the low binding energy side of the $3d_{5/2}$ peak, i.e., 1171 eV. In Fig. 3 the starting point was set at the high binding energy side of the KVV peak, i.e., 997 eV, and the end point to the local intensity min-