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Influence of substrate roughness on the layering of particles in nanocermet thin films

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Abstract
The morphology of nanocermet thin films deposited on substrates having different roughnesses has been studied by surface sensitive x-ray scattering techniques. Grazing incidence small angle scattering data of the films shows that the nanoparticles, which are present in the ceramic matrix, exhibit a specific average interparticle separation. Analysis of the x-ray reflectivity indicates that, in the films deposited on smooth substrates, the nanoparticles adopt some layering along the growth direction. This layering tends to diminish with increasing substrate roughness and vanish completely for very high substrate roughness. The variation of such layering with substrate roughness is an indication that it starts close to the substrate and is an effect of the substrate boundary condition.

1. Introduction

Ceramic thin films containing nanoparticles are interesting materials for the development of new technological devices. Physical properties, namely optical, electrical, magnetic properties etc, of such materials are different from those of the bulk composite materials [1]. The difference is mainly due to the confinement effect [2] of the nanoparticles in the ceramic matrix. This effect, which arises from the finite size of the nanoparticles, is also related to the shape and distribution of the particles in the matrix. It is therefore crucial to understand the morphology and distribution before determining the physical properties of such films.

The surface sensitive x-ray scattering technique plays an important role in determining the growth [3] and morphology [4] of thin films in a non-destructive way. In particular, specular reflectivity measurement provides information regarding the electron density profile (EDP) of the thin films along the growth (z) direction [5]. Diffuse scattering measurements using point and two-dimensional (2D) detectors yield information about large in-plane correlated features [6] as well as small correlated features other than the ones observed in the z-direction [7]. A combination of specular reflectivity and diffuse scattering measurements in a wide angular range has been used recently to understand the morphology of Pt–Al_2O_3 nanocermet thin films deposited on very flat glass substrates [8]. In these films, the crystalline Pt nanoparticles are found to be distributed in the alumina ceramic matrix with an average separation, but a preferential layering of the particles occurs close to the substrate along the growth direction. It was inferred that the layering could be related to the presence of a smooth interface between the substrate and the film itself. In this paper we present the morphology of three nanocermet thin films deposited on substrates having very different roughness to provide further evidence that the layering of nanoparticles at the film–substrate interface is related to the smoothness of the substrate.

2. Experiment

Cermet films of Pt–Al_2O_3 were made by co-sputtering amorphous Al_2O_3 with metallic Pt on float glass substrates. Three films labelled PAGL, PAGM and PAGH were deposited on float glass presenting low, medium and very high substrate roughness, respectively. All other parameters were kept identical for the three films during the growth process. Mechanical polishing was used to modify the native roughness of the float glass and atomic force microscopy was carried

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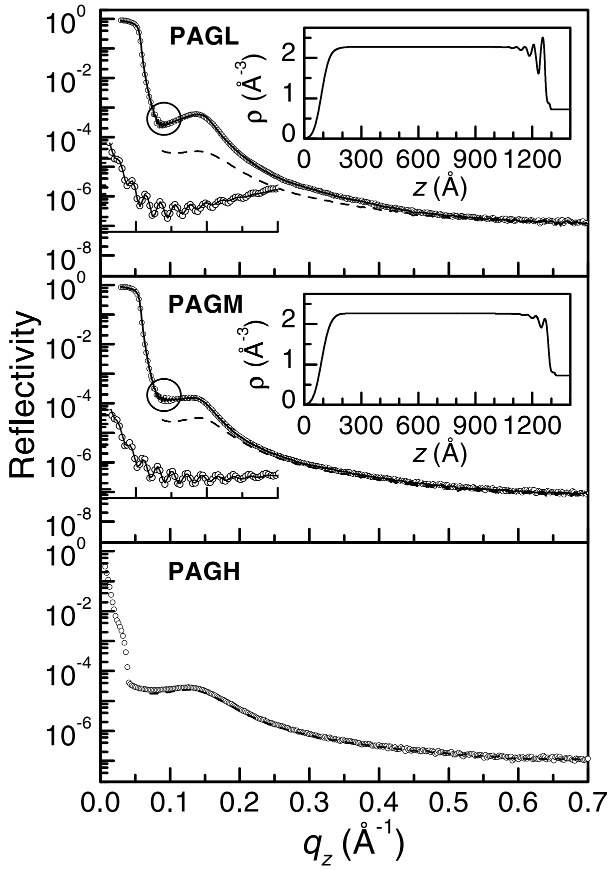

Figure 1. Reflectivity (○) and longitudinal diffuse scattering (– – –) data of the three nanocermet thin films in three different panels. Full curves passing through the reflectivity data of the top two panels are the best fit curves obtained for the EDP shown in the inset (top right) of each panel. An enlarged view of the selected portion of the reflectivity curves along with the fitting are plotted in the inset (bottom left) of the top two panels to show the Kiessig fringes due to the total film thickness.

out to probe this modification in a quantitative way before deposition. The roughness was found to be about 4, 9 and 3400 Å for the substrates of the PAGL, PAGM and PAGH films, respectively.

X-ray specular reflectivity, longitudinal and transverse diffuse scattering were performed using a laboratory source (Philips diffractometer) of wavelength 1.54 Å. Grazing incidence small angle x-ray scattering (GISAXS) measurements of the films were performed using a synchrotron source (D22 beam line, LURE) at energy 7 keV and the reciprocal space maps were collected with a 2D detector. Details about the measurements geometry and techniques are published elsewhere [8].

3. Results and discussion

The specular x-ray reflectivity and longitudinal off-specular (off-set 0.12°) scattering are shown in figure 1. Off-specular curves for the three films exhibit almost the same shape; namely only a broad hump near $q_z = 0.131$ Å^{-1} is present. The specular reflectivity for the three films, on the other hand, is different. For PAGL and PAGM films, the total external reflection plateau is clearly visible and it is followed by Kiessig fringes and a broad hump near $q_z = 0.131$ Å^{-1}. The Kiessig fringes, which give an indication of total film thickness, are clear in the enlarged view (inset of figure 1) of the selected portion of the reflectivity curves. On the contrary, no total external reflection or Kiessig fringes are observed for the PAGH film. This indicates that the very high roughness of this film prevents the observation of a specular reflection, which in turn impedes the estimation of the total film thickness. Although the broad hump near $q_z = 0.131$ Å^{-1} is present in the specular measurements from all films, its intensity decreases with the increase of the substrate roughness. In particular, the intensity of this hump for the PAGH film is exactly the same in the specular and off-specular directions. This shows that such a film does not present any true specular component but only diffuse scattering.

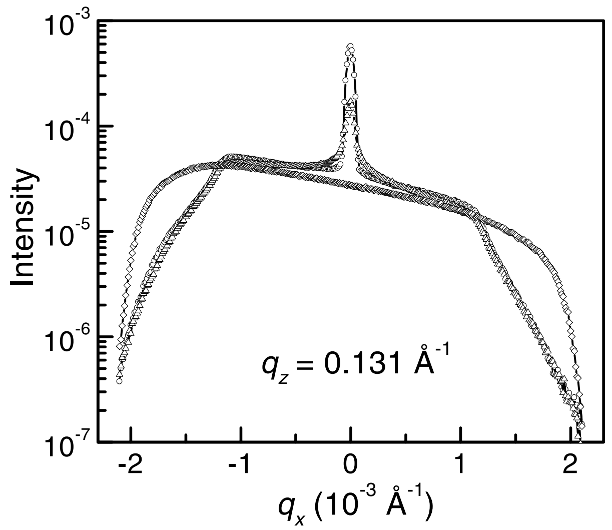

Figure 2. Transverse diffuse scattering of the three (○, PAGL; △, PAGM; and ◇, PAGH) nanocermet thin films indicating how the specular component changes with the substrate roughness.

The transverse diffuse scattering data measured at $q_z = 0.131$ Å^{-1} (where the broad hump is observed in reflectivity curves) are shown in figure 2 for the three films. A sharp specular central component dominating the low diffuse scattering is shown for the PAGL film, while there is only diffuse scattering for the PAGH film. It can be noted that with the increase of substrate roughness the specular component decreases and even vanishes while the width of the diffuse scattering increases. This clearly indicates that the substrate–film interface roughness has a major influence on the ratio between the specular and diffuse component.

To obtain information in different directions of the film, we mapped out the reciprocal space by carrying out GISAXS measurements. Images of three films shown in figure 3 are all alike, as is the case for longitudinal diffuse scattering (figure 1). The absence of a highly intense region close to the centre for the PAGH film is related to the absence of a definite specular direction on the length scale of the x-ray probe. The annular ring, which is the main feature present in the three images, is related to the heterogeneous structure of the film. In particular, it indicates the presence of high electron density regions exhibiting almost the same average separation in any

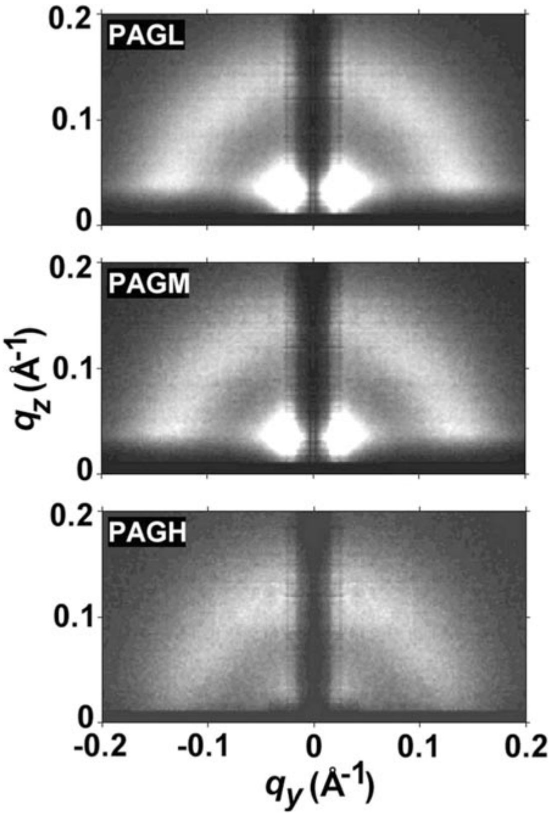

Figure 3. GISAXS images of the three nanocermet thin films collected at a fixed incident angle. The annular ring observed in all the images is related to the separation between clusters in the films.

direction. However, the intensity of the annular ring depends on the roughness of the substrate. For PAGL and PAGM films, the ring has almost the same intensity in any direction. For the PAGH film, the situation is very different; the intensity in the in-plane direction ($q_z \to 0$) is less compared to that of the out-off-plane direction. With a roughness of ∼3400 Å one can expect a decrease of the effective number of scatterers per unit area when looking in the plane of a film. The electron density of a heterogeneous thin film, in which metallic clusters are randomly distributed in the amorphous matrix, can be written as [9]

$$\rho(r) = \left[\rho_{matrix} + \Delta\rho \sum_i \delta(r - r_i) \otimes S_{cluster}(r_i)\right] S_F(r) \quad (1)$$

where $\Delta\rho = \rho_{cluster} - \rho_{matrix}$, $S_{cluster}(r_i)$ is related to the shape and size of the ith cluster at a position r_i and $S_F(r)$ is related to the finite dimensions of the film. If we consider spherical clusters of radius R, distributed in the matrix according to a cumulative disorder with average separation d, the diffuse intensity arising from the clusters is [8]

$$I_{cluster} \propto \frac{(\sin qR - qR\cos qR)^2}{(qR)^6} \times \frac{1 - e^{-2q^2\sigma_d^2}}{1 - 2\cos(qd)e^{-q^2\sigma_d^2} + e^{-2q^2\sigma_d^2}} \quad (2)$$

where σ_d is the variance of d. Equation (2) has been used to obtain the value of R and d from the GISAXS and longitudinal off-specular scattering data. It was found that the average particle size ($2R$) is ∼26 ± 4 Å while the average particle separation (d) is 45, 45 and 49 Å for PAGL, PAGM and PAGH films, respectively. The present analysis shows that the size of the nanoparticles is almost the same while the average separation for the film deposited on a high roughness substrate slightly deviates from that of the other two films. These results can be understood in the following way. The size of the nanoparticles is not related to the substrate roughness but to the deposition conditions. Since the deposition conditions are the same for all the films, one expects no appreciable change in the average particle size. The same is true for the average separation of the nanoparticles except for those particles close to the substrate. The key parameters, which are going to govern the position of these particles, will be the ratio of the correlation length ξ of the substrate roughness to the diameter $2R$ of the nanoparticles and the roughness σ of the substrate. If σ is small compared to $2R$, the average separation will not be affected, whatever ξ. On the other hand, if σ is very large and $\xi \gg 2R$ then the particle separation will be influenced by the topology of the substrate.

Now we consider again the specular reflectivity where major differences with substrate roughness have been observed. We wish to address how the film morphology is modified along the growth direction. To get quantitative information we calculate the reflectivity of the PAGL and PAGM films using a matrix technique. Different EDPs were used to calculate the reflectivity from which it was obvious that it was needed to introduce some oscillatory region to produce the hump in the reflectivity curve. We also found that best fits were obtained when the oscillations were close to the substrate as reported earlier [8]. It can also be argued from the shape and intensity of the peaks at $q_z = 0.131$ Å^{-1} (both for specular and transverse) that oscillation is only needed in a small portion of the EDP. If it is close to the film–air interface then such formation of layering should not depend upon small changes (∼5 Å, for PAGL to PAGM) in substrate roughness. Damped oscillatory EDPs were therefore used to fit the two reflectivity curves and the best fits along with the EDPs are shown in figure 1. The EDP shows that both films have high top surface roughness (∼34 Å) and nearly the same total film thickness (∼1250 Å). The oscillation close to the substrate, which is also found in both EDP is, however, more contrasted for the PAGL film. The damped oscillation in the EDP can be explained in terms of some cumulative disorder in the layering of nanoparticles. The high electron density close to the substrate (prominent for PAGL film) is related to the layering of particles (i.e. the large number of Pt particles in a given x–y plane) while the period of oscillation (∼47 Å) is related to the average particle separation along the growth direction. The growth of the film starts from the substrate and a smooth boundary condition (low substrate roughness) helps to form most of the nanoparticles in a given x–y plane [8]. However, changing this boundary condition by increasing the substrate roughness has the effect of reducing the number of nanoparticles in a given x–y plane. The contrast of the oscillation in the EDP consequently decreases as observed in the PAGM film. When the distance to the substrate increases, the boundary condition imposed by the substrate on the nanoparticles is progressively relaxed after a few layers and a film of constant average electron density is finally observed.

4. Conclusions

The morphologies of Pt–Al_2O_3 nanocermet thin films deposited by rf sputtering on float glass of different substrate roughnesses have been studied by x-ray scattering techniques. It is shown that, whatever the substrate roughness, Pt nanoparticles (of size ∼26 Å) with average separation (∼45–49 Å) are present in the films of alumina matrix. However, there is a significant change in the morphology of the film in the growth direction with the substrate roughness. In particular, the layering of nanoparticles, which is observed in films deposited on substrates of low and medium roughness, disappears in the film deposited on a very high rough substrate. This strongly suggests that the layering mainly occurs close to the substrate and only for smooth enough substrates. It will be interesting to work out the exact relationship between roughness (σ), correlation length (ξ) and particle size ($2R$) with layering for metal nanoparticles in a different matrix. Further work in this direction with a systematic variation of the above parameters may hopefully be able to establish this.

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