Preparation of metal oxide nanoparticles by gas aggregation cluster source

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ABSTRACT

Al/Al_xO_y and Ti/TiO_x nanoparticles have been fabricated using gas aggregation cluster source (GAS) equipped with 3-inch planar magnetrons. The main attention has been devoted to the evaluation of the role of oxygen admixture on the deposition rate and properties of formed nanoparticles. It has been found that oxidized nanoparticles are deposited when oxygen is present in the working gas mixture. Highest deposition rates for production of Al/Al_xO_y or Ti/TiO_x nanoparticles were observed when 3% or 1.5% oxygen was present in the working gas mixture, respectively. Mean diameters of about 16 nm for the Al_xO_y nanoparticles and 30 nm for TiO_x have been found under these deposition conditions.

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1. Introduction

The fabrication of metal oxide nanoparticles (NPs) receives nowadays increasing attention. The main reason of this is a huge application potential of such materials that covers for instance water treatment, cosmetics, medicine, photovoltaic, semiconductor packing materials, fuel cells or catalysts [1—4]. Probably the most studied metal oxide NPs are titanium oxide that are employed in cosmetics, food, paints, personal care products or photovoltaic applications [5—7] and aluminium oxide NPs that are used in high-performance materials to increase their ductility, scratch resistance and toughness [8]. Another perspective field, where alumina NPs are expected to play an important role, is their use for production of antimicrobial materials [9].

Although nanoparticles may be produced by techniques based on purely chemical synthesis (e.g. Ref. [10]), there is a growing interest in methods utilizing vacuum technologies, such as for example vacuum evaporation or sputtering at elevated pressures (typically tens to hundreds of Pa). Under these conditions the NPs are formed by sputtered vapour in the gas phase as the result of three step process that consist of nucleation, coagulation and attachment of atoms and ions onto created NPs. A recent example of this approach is nanoparticle synthesis by highly ionized plasmas produced by high power pulsed hollow cathode [11]. It was reported that the size distribution of produced NPs can be tuned in certain range by adjusting the pulse parameters, such as frequency, pulse width, or peak current [12]. An alternative approach is based on the use of gas aggregation sources (GAS) of nanoparticles. In this case the magnetron is inserted into a cooled aggregation chamber that is separated from the rest of the deposition chamber by a small output orifice [13]. This arrangement assures sufficiently high pressure in the aggregation chamber needed for the effective production of NPs that are subsequently dragged by working gas through an output orifice into the vacuum deposition chamber and reach the substrate in the form of a nanoparticle beam. The key advantage of GAS is complete separation of the NPs production from the rest of the deposition chamber, which facilitates combination of GAS with other vacuum based techniques of material deposition. This in turn makes it possible to produce either nanostructured coatings by overcoating NPs by a thin film of the same or other material (e.g. Refs. [14—16]), use NPs as seeds for formation of columnar structures prepared by glancing angle deposition [17] or various kinds of nanocomposite materials (e.g. Refs. [18,19]).

Different GAS systems were already identified as reliable and highly effective sources for deposition of metallic NPs such as Ag, Cu, Pt, Ti or Al (e.g. Refs. [18—26]) or plasma polymerized NPs (e.g.

Refs. [27,28]). In addition, it was shown that gas aggregation sources may also be used for production of metal-oxide NPs (e.g. Refs. [23,29–33]). Two strategies were followed. In the first one, the metallic nanoparticles are after the deposition oxidized on ambient air (e.g. Ref. [29]). However, the necessity of the oxidation step makes this approach not suitable for combination of GAS with other vacuum based deposition methods needed for instance for production of nanocomposites. Because of this, there were attempts to produce metal-oxide NPs directly in the GAS. In this case small amount of oxygen was added to the inert working gas [30–33]. According to the reported results, the presence of oxygen influences not only the chemical structure of produced NPs, but it has also strong impact on the deposition rate and the stability of NPs formation. The main objective of this study is to evaluate the influence of amount of added oxygen on the process of TiO_x and Al_xO_y NPs formation. In order to meet this aim, the measurements of deposition rate of NPs were accompanied by optical emission spectroscopy of plasma inside the aggregation chamber as well as by evaluation of chemical composition and sizes of NPs produced at steady-state condition.

2. Materials and methods

The scheme of apparatus used for production of Al_xO_y nanoparticles is depicted in Fig. 1. It consisted of a gas aggregation source, which was attached onto a deposition chamber pumped by rotary and diffusion pumps to a base pressure 10^{-4} Pa. The used GAS was based on stainless steel cylindrical aggregation chamber (diameter 110 mm, length 450 mm) ending in an orifice 3 mm in diameter. The source of material for nanoclusters production was DC, water-cooled, planar, 3-inch magnetron equipped with 3 mm thick Al target (purity 99.99%) that was operated in constant current mode (200 mA). The distance between the target and the output orifice was 150 mm and was kept constant during all experiments. The aggregation chamber was equipped with diagnostic ports that enabled us to monitor plasma composition during the deposition of nanoclusters by means of optical emission spectroscopy (AvaSpec-3648-2-USB2). In addition, the magnetron and exit orifice can be moved against diagnostic ports during the deposition (i.e. in-situ) while keeping the constant distance of 15 cm. This is a special "diagnostic" variation of our simple GAS that enables e.g. OES measurements in an arbitrary part of the aggregation chamber.

Similar GAS was used for production of Ti and TiO_x nanoparticles. In contrast to the source employed for fabrication of Al_xO_y NPs the aggregation chamber of this system was not moveable and the diagnostic ports were thus at a fixed 3 cm distance from the 3-inch magnetron. The diameter of the output orifice was 1.5 mm and all experiments reported in this study were performed at constant applied 300 mA DC current.

Argon (99.99%) with an admixture of oxygen (up to 20%) was used in both cases as working gas. The flow of Ar (6 sccm in case of Al/Al_xO_y NPs and 1.5 sccm in case of Ti/TiO_x NPs) was regulated by flow controller (MKS), while the amount of oxygen was tuned using a calibrated needle valve (Pfeiffer). The total pressure in the gas aggregation chamber was kept constant and equal to 40 Pa in experiments with Al and Al_xO_y NPs and 28 Pa in case of Ti an TiO_x NPs. The pressure in the main deposition chamber was 0.1 Pa.

The deposition rate of produced NPs was measured by a quartz crystal microbalance. Chemical composition of produced nanoparticles was determined by means of X-ray Photoelectron Spectroscopy (XPS, Phobios 100, Specs) performed in-situ, i.e. without exposing produced NPs films to the ambient atmosphere. Spectra were acquired at constant take-off angle of 90° using Al Kα X-rays source (1486.6 eV, 200 W, Specs). Wide spectra were acquired for binding energies in the range of 0–1100 eV at a pass energy of 40 eV (dwell time 100 ms, step 0.5 eV). High resolution spectra were obtained at pass energy of 10 eV and were charge referenced to adventitious carbon at 285.0 eV. Spectral analysis was performed using CASA XPS software. Finally, scanning electron microscopy (SEM, Tescan Mira 3) was used for the study of morphology of deposited coatings.

Adhesion of NPs to Si/SiO_2 substrates was studied by an AFM (Ntegra Prima, NT-MDT) both in a semi-contact and in a contact mode using diamond-like-carbon coated cantilevers (ContDLC, NanoandMore) with a guaranteed tip radius of 15 nm. The spring constant of 0.26 N/m was measured by the Sader method and the cantilever deflection detection system was calibrated before the measurements as described in Ref. [34]. First, the surface of the sub-monolayer of the NPs was scanned in the semicontact mode to identify an individual particle to be studied. Then the AFM was switched to the contact mode and the profile of the particle was continuously scanned with the increasing contact force until it was moved away. Finally, the AFM was switched back to the semi-contact mode and the entire area was scanned again to confirm that the particle was removed.

3. Results and discussion

3.1. Al and Al_xO_y nanoparticles

The first goal of this study was the identification of optimum experimental conditions which would provide stable and effective deposition of alumina nanoparticles. It was found that at constant magnetron current and pressure in the aggregation chamber, the deposition rate of NPs is strongly dependent on the used working gas mixture.

First, it was observed that the presence of oxygen significantly improves the stability of the process of formation of nanoparticles (see Fig. 2): whereas in case of using Ar/O_2 working gas mixture the amount of deposited NPs increased almost linearly with deposition time over the period of more than 30 min, the deposition rate, in agreement with a previous study [19], gradually decreased and finally stopped after prolonged operation time when only pure Ar was used.

Further experiments were performed after both the plasma parameters (magnetron voltage, intensity of emission spectral lines) and the deposition rate were stabilized. The temporal instabilities of deposition process in the initial period, observed also in previous studies in case of Ti NPs [31], lasted typically 20–30 min depending on the deposition conditions and the history of the magnetron. After this phase the deposition rate, magnetron voltage
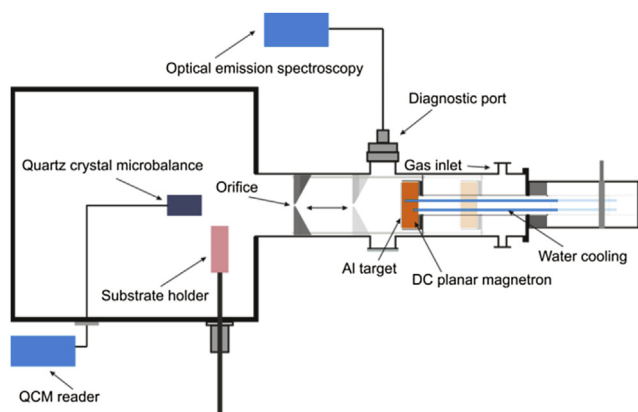

Fig. 1. Scheme of deposition set-up with moveable gas aggregation source used for Al and Al_xO_y NPs.