Aluminium oxide clusters and their nanocomposites with plasma polymers prepared by a gas aggregation cluster source and plasma polymerization.

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Abstract: Al/AlxOy nanoclusters were prepared by means of a gas aggregation cluster source (GAS) following a Haberland concept. Nanoparticles of 40-60 nm in diameter were formed and extracted by Ar flow through a nozzle which separated the GAS and the vacuum deposition chamber. For embedding the nanoclusters into a polymeric matrix, an auxiliary RF magnetron was mounted in the vacuum deposition chamber perpendicularly to the direction of the cluster beam. The auxiliary discharge was operated in the Ar/n-hexane gas mixture to produce hydrocarbon plasma polymer matrix co-deposited with Al/AlxOy nanoclusters. Prepared metal clusters and their nanocomposite thin films were characterized by means of Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) to determine the size of the clusters and the surface roughness of the nanocomposite thin films. Chemical composition of the films was investigated by X-ray electron spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: metal clusters, plasma polymer, nanocomposite thin films

Introduction

Nanostructured and nanocomposite materials are used in many current and emerging technologies. In particular, profound interest is in nanocomposites consisting of metal and metal oxide nanoparticles embedded into a polymer matrix due to their novel functional properties [1]. The nanocomposites can be prepared by a variety of different deposition methods. One of them is a simultaneous plasma polymerization and metal sputtering. In this case, magnetron sputtering of metals is performed in a mixture of an inert gas and an organic precursor. Magnetron sputtering produces the flux of atomic metal whereas plasma polymerization of the organic precursor results in growth of a plasma polymer. Formation of the metallic nanoparticles dispersed in plasma polymer matrix occurs on the substrate and it strongly depends on the mixing conditions. The process has two principal drawbacks: first, the chemical reactions between the atomic metal and the organic species could occur during the deposition on the substrate, thus, preventing the formation of metal nanoparticles; second, it is impossible to control independently the size and amount of metal inclusions in the matrix. For such cases, it would be necessary to form metal nanoparticles with required characteristics in a separate process and then transport them onto the substrate where mixing with plasma polymer occurs. It can be easily done by a co-deposition system consisting of an independent source of metal nanoparticles and a source for plasma polymer matrix. Changing independently the deposition parameters for metal clusters and for plasma polymerization the nanocomposites with different structure and properties can be

deposited. In this work we focus our attention on Nanocomposite Al(AlxOy)/plasma polymer films.

Experimental

The experiments were carried out in a stainless steel vacuum chamber pumped down by rotary and diffusion pumps to a base pressure
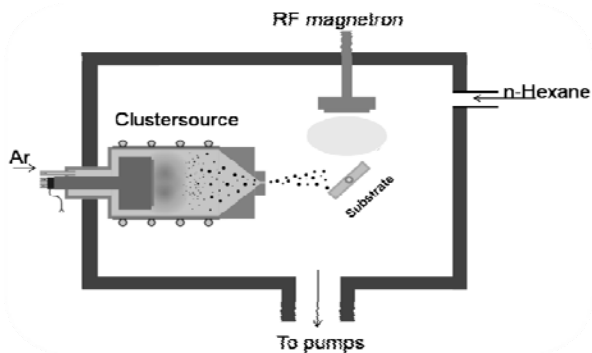
Figure 1. Schematic drawing of the deposition chamber used for the preparation of nanocomposite thin films.

of 10^{-4} Pa. Schematic drawing of the deposition system is shown in the Fig. 1.

Al/AlxOy cluster deposition

Al nanoclusters were produced by the Gas Aggregation cluster Source described in [2-5].

Briefly, it is based on a planar magnetron 80 mm in diameter placed in the aggregation chamber, both cooled with water. The aggregation chamber ends with an exit cone with an orifice of 1.5mm in diameter. A DC power supply (AE MDX 1.5K) operated in the constant current mode (0.2A) was used for sputtering of aluminium from a 2mm thick target. Argon at pressure of 25 Pa was used as a working gas in the GAS. Sputtered Al atoms nucleate(condense) into custers while necessary cooling is provided by collisions of surrounding argon atoms followed by cluster growth until a balance is reached. Clusters are then extracted by the Ar flow through the orifice to the vacuum chamber.

Deposition of nanocomposite thin films

The flux of Al clusters was directed onto the substrates where hydrocarbon (C:H) plasma polymer was growing. An RF planar magnetron equipped with a graphite target was used as a source of plasma polymer matrix. The magnetron was placed in the vacuum chamber perpendicularly to the cluster source as shown in Fig. 1. The power of 30W was applied from the R.F. generator (13.56 MHz Dressler Ceasar). R.F. discharge was ignited in the vacuum chamber at pressure of 0.5Pa in Ar/n-Hexane gas mixture with concentration ratio of 1/3. The deposition rate of C:H plasma polymer was about 20-25nm/min.

Al/Al$_x$O$_y$ nanoclusters and their nanocomposites were deposited on different substrates (Si wafer, glass, gold coated glass) placed inside the vacuum chamber at the angle of 45 degree with respect to both the RF magnetron and the cluster source as depicted in Fig. 1. The distances from the substrates to the cluster source and the RF magnetron were 20 cm and 10 cm, respectively.

Samples characterization

Scanning electron microscope (MIRA III Tescan) and Atomic force microscope (NT-MDT Ntegra) were utilized to characterize the surface topography, cluster size and their distribution. The film thickness was determined by ellipsometry (Woollam M-2000). The chemical composition of the nanocomposites was investigated by XPS (Phobios 100, Specs) and FTIR (Bruker Equinox 55).

Results and discussion

Al clusters

At first step, the Al clusters were deposited and characterized. Fig. 2a shows the typical thin film of aluminium nanoclusters. The size distribution of Al clusters is very narrow and the

diameters of the particles lie in the range of 40-60 nm. The deposited films are very porous.
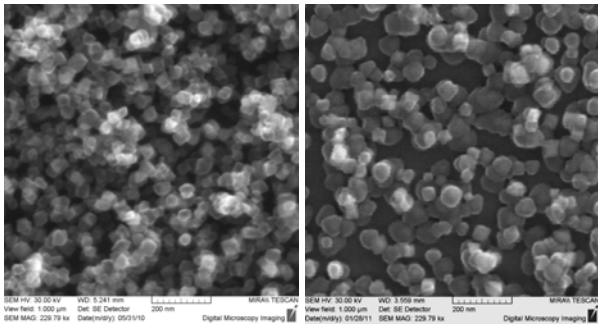
Figure 2. The SEM images of: a) Al clusters prepared by the GAS (pressure 25 Pa, magnetron current 0.2 A); b) Al/C:H nanocomposite thin film prepared by co-deposition (Al cluster deposition: 0.2 A, 25 Pa; C:H deposition Ar:Hex=1:3, work pressure 0.5 Pa, RF power 30 W).

Thin films of Al clusters were found to have low adhesion to any kind of substrate (clusters can be easily wiped from the substrate). In order to solve this problem, Al clusters were embedded into a polymer matrix. The SEM image of this nanocomposite thin film is shown in the Fig 2b. Both SEM images (Fig 2a and 2b) reveal that the metal clusters embedded into the polymer matrix appear to be larger than those without polymer matrix, such increase given by thickness of the plasma polymer.

The surface topography of the nanocomposites Al/C:H was observed by AFM.
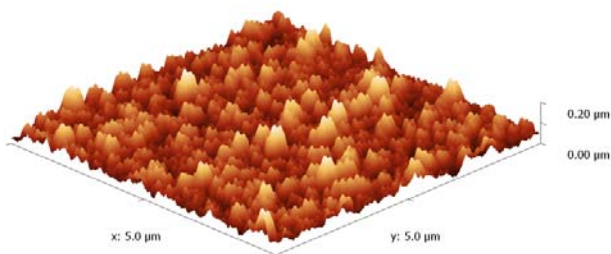
Figure 3. The AFM image of the Al/C:H thin film prepared by co-deposition. (Al cluster deposition: 0.2 A, 25 Pa; C:H deposition Ar:Hex=1:3, work pressure 0.5 Pa, RF power 30W)

The relatively high roughness was observed (RMS is about 25-30nm at 5 μm scan size). This is illustrated in Fig. 3 which shows the 3-D AFM image of the nanocomposite.

In order to determine the chemical structure of the nanocomposites the FTIR-RAS spectroscopy was employed. The usual structure of hydrocarbon plasma polymer can be easily recognized (Fig. 4) [2, 6]. The most intensive bands in the spectral range of 2870–2960 cm^{-1} correspond to stretching vibrations of the CH$_2$ and CH$_3$ groups.
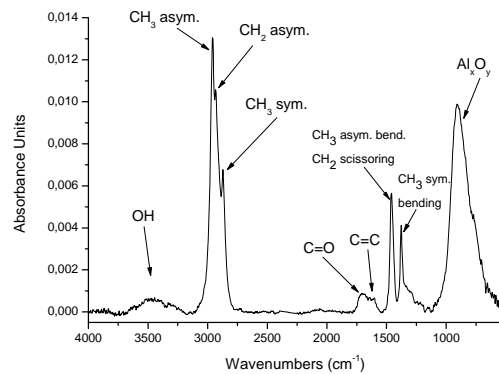
Figure 4. The FTIR-RAS spectrum of the Al/CH nanocomposite thin film prepared by co-deposition (Al cluster deposition: 0.2 A, 25 Pa; C:H deposition Ar:Hex=1:3, work pressure 0.5 Pa, RF power 30W)

The CH structure can be seen also from the peaks at 1460 cm^{-1} (unresolved CH$_2$ scissoring and CH$_3$ asymmetrical bending) and at 1370 cm^{-1} (CH$_3$ symmetrical bending). The bands at 1700 cm^{-1} and near 1620 cm^{-1} correspond to the C=O and C=C groups, respectively. The wide absorption peak from 700 cm^{-1} to 1000 cm^{-1} comes from Al particles embedded into plasma polymer matrix. This band is not fully recognized but most probably it corresponds to Al-O stretching vibrations. The presence of OH and C=O peaks shows a certain degree of oxidation in the nanocomposites.

The elemental composition of the surface was investigated by XPS. Only 2% of Al was detected while the concentration of C and O was

89% and 9%, respectively. The low concentration of aluminium is caused by the fact that the Al clusters are covered with plasma polymer and they can be hardly seen by highly surface sensitive XPS (the sampling depth is 10 nm). High resolution XPS Al2p spectra show that 30% of Al is present in the metallic form. Taking into account the exponential attenuation of the XPS signal with sampling depth, the real content of metallic aluminium in the clusters should be significantly higher. This means that the Al clusters are slightly oxidized and are covered with a few nanometers of aluminium oxide layer originated by residual gases in the chamber and partial oxidation of the target.

Conclusions

Al/AlxOy nanoclusters of 40-60nm in diameter can be prepared using the simple gas aggregation cluster source based on the magnetron sputtering. To solve the problem of low adhesion to the substrate, clusters can be embedded into the plasma polymer matrix. The surface of nanocomposits prepared by co-deposition of Al clusters and polymer matrix is very rough. At least 30% of aluminium in the clusters is present in metallic form.

Acknowledgements

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