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Immersion of low-energy deposited metal clusters into poly(methyl methacrylate)

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ABSTRACT

Immersion of size-selected metal clusters deposited on thin poly(methyl methacrylate) (PMMA) films is studied. Clusters are produced by magnetron sputtering and soft-landed on the polymer substrates. It is found that thermal annealing at temperatures above the polymer glass transition point facilitates embedment of the deposited nanoparticles (NPs) into PMMA. The immersion degree can be controlled by the annealing time. Together with the control of cluster coverage by tuning the deposition time, the described approach represents an efficient method for the formation of thin polymer composite layers with embedded size-selected metal NPs. In the case of silver, the composite films demonstrate excellent plasmonic properties. However, the thermal annealing is found to quench the plasmon resonance of copper NPs. It is suggested that oxidation under elevated temperatures is the most probable mechanism destroying the plasmonic properties of the copper NPs. A simple treatment method by ozone is proposed to form an oxide shell around the metal core, thus, protecting the core against environmental factors causing degradation of the plasmonic properties.

1. Introduction

Polymer films with embedded metal nanoparticles (NPs) are of significant interest due to a number of applications in research and industry [1,2]. This includes different possibilities. (i) To control conductivity by varying a metal filling factor in polymers, thus, allowing to tune the charge carrier transport from variable range hopping towards percolation and insulator-to-metal transition [3–5]. (ii) To form media with ferromagnetic single domain behaviour or superparamagnetism [6,7]. (iii) To synthesise polymer composites utilizing localised surface plasmon resonance (LSPR) of noble metal NPs [8] giving rise to applications in sensor technologies [9,10], fabrication of plasmon resonators demonstrating enormous enhancement of quantum emitter's fluorescence [11,12], thus, facilitating the development of ultra-bright and stable single-photon sources. (iv) To produce antibacterial coatings which are essential for medicine and food technologies [13].

There are different approaches for the formation of metal/polymer composites among which are vapour phase deposition, wet chemistry, ion implantation and some others [14]. All these techniques have their advantages and disadvantages. For example, ion implantation provides a possibility to fill polymers with practically any metal and control its concentration [2,15,16]. However, to nucleate NPs high fluences are required that leads to radiation damage of the polymer matrix and changes of its composition [2,17–20]. Poor control of particle sizes and a relatively wide spread of NPs in depth due to straggling of ion projected ranges are other disadvantages [16,21].

Recently, it has been demonstrated that the cluster beam technique is an efficient method for embedment of metal NPs into polymers [22,23]. The advantages of this approach are (i) in very good control of cluster composition due to the formation in vacuum from pure targets, (ii) a possibility to tune particle sizes prior the deposition or embedding and (iii) in the ability to vary the impact energy [24]. This approach provides fascinating capabilities for the formation of polymer films filled by NPs and these composites demonstrate tunable optical and electrical properties [25,26]. However, the mechanisms governing cluster immersion and properties of embedded NPs require better understanding as well as methodologies to control this process need to be further developed for the synthesis of polymer composites with desired properties.

In the current work, size-selected copper cluster ions produced by magnetron sputtering cluster apparatus (MaSCA) are deposited in the low-energy regime on poly(methyl methacrylate) (PMMA) films prepared by spin-coating. The experiments have shown that NP immersion can be driven by thermal annealing, thus, opening

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great capabilities to form metal/polymer nanocomposites with properties attractive for practical applications. The results are compared with the previous work on the embedding of silver clusters into PMMA [23].

2. Experimental

Metal clusters are produced using MaSCA. Schematic drawing of the apparatus is presented in Fig. 1. For cluster production, a commercial source (NC200U, Oxford Applied Research) is utilized. In the source, a metal target of 99,99% purity is sputtered, clusters are formed and expanded into the source chamber through the nozzle. Thereafter, they are collimated into a beam by the conical in shape skimmer and steered into the electrostatic quadrupole mass selector (EQMS). The clusters in the source are formed in different sizes; a significant fraction of them is ionized that allows mass (size) selection by electrostatic fields as earlier described in [27]. The experiments with silver have demonstrated that the standard deviation of the particle diameters within 7% is achieved for optimized EQMS parameters [23]. The results of size-selection for copper particles deposited on Si substrate are shown in Fig. 2 demonstrating very similar values of standard deviation (6–9%), thus, confirming reliability of size selection for different metals.

The current work is focused on the study of copper clusters and the results are compared to those earlier obtained for silver ones [23]. Size-selected negatively charged copper cluster ions are soft-landed on substrates with PMMA film in the deposition chamber with the background pressure of ca. 5×10^{-7} mbar. The clusters are selected using voltage $U_{QP} = \pm 500$ V resulting in NPs with mean diameters of 15 nm as follows from the curve presented in Fig. 2. Typical coverages used in the experiments are below a monolayer of NPs. Polymer films are prepared by a standard spin coating procedure on quartz substrates from 1% solutions in chlorobenzene (molecular weight 950K PMMA C 9 from MicroChem). The films are produced in 50 nm thicknesses and annealed in ambient atmosphere at 100 °C for 10 min. to solidify them and evaporate remaining solvents. After the cluster deposition, the samples are annealed again at 120 °C for 10 min. This temperature is above the glass transition point of PMMA (105 °C) allowing to increase viscoelasticity of the material and "chain mobility" favoring embedment of NPs into the films [14].

Surface morphology of the samples with supported NPs is studied by atomic force microscopy (AFM) in tapping mode using Ntegra Aura nanolaboratory (from NT-MDT). Commercial cantilevers with sharp silicon tips (radius of curvature < 10 nm) are used.

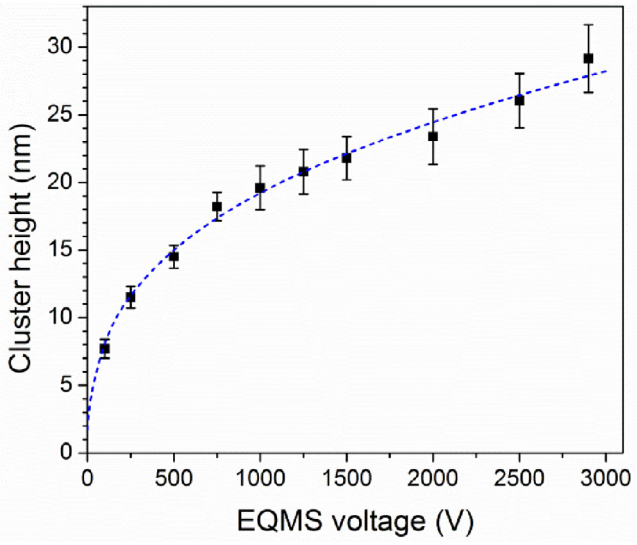

Fig. 2. Measured by AFM height of Cu clusters deposited on Si substrate versus voltage applied to EQMS. Error bars show standard deviations of cluster height.

The extinction spectra are obtained from transmission measurements using a double beam Perkin Elmer High-Performance Lambda 1050 Spectrometer in standard configuration.

3. Results and discussion

AFM images of the samples with as-deposited copper clusters and after the annealing are presented in Fig. 3. The height of NPs after the annealing is decreased indicating partial immersion of the clusters into PMMA. This phenomenon was studied in detail in our previous work with silver and NPs embedment was directly confirmed by cross-sectional transmission electron microscopy [23]. It was also shown that the degree of immersion can be controlled by the duration of thermal annealing. According to the theory presented elsewhere [14,28], the driving force for this process is a large difference in surface free energy (surface tension) between metals and polymers. For example, surface tension (γ) is known to be ≈ 1200 mJ/m^2 for silver, 1650 mJ/m^2 for copper, while $\gamma \approx 30$–40 mJ/m^2 for PMMA [29,30].

Extinction spectra of the samples with copper NPs on/in PMMA are shown in Fig. 4. The spectra for as-deposited clusters demon-

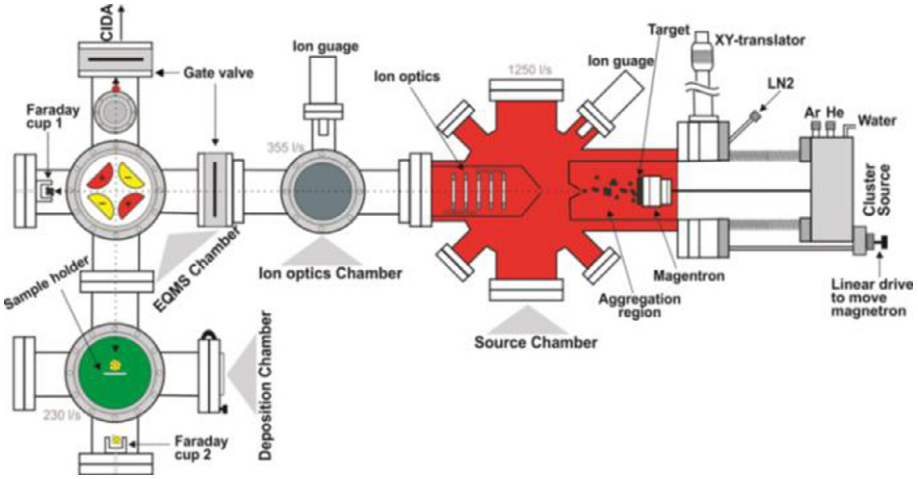

Fig. 1. Schematic view of MaSCA.

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