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Published in:
MRS Advances

DOI (link to publication from Publisher):
10.1557/adv.2018.427

Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

Link to publication from Aalborg University

Citation for published version (APA):
Ceynowa, F. A., Chirumamilla, M., Zenin, V., & Popok, V. (2018). Arrays of Size-Selected Metal Nanoparticles Formed by Cluster Ion Beam Technique. *MRS Advances*, *3*(45-46), 2771-2776. https://doi.org/10.1557/adv.2018.427

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DOI: 10.1557/adv.2018.427

Arrays of Size-Selected Metal Nanoparticles Formed by Cluster Ion Beam Technique

Florian A. Ceynowa[1,2], Manohar Chirumamilla[1], Vladimir A. Zenin[3] and Vladimir N. Popok[1]

[1]*Aalborg University, 9220 Aalborg, Denmark*

[2]*Kiel University, 24098 Kiel, Germany*

[3]*University of Southern Denmark, 5230 Odense, Denmark*

ABSTRACT

Deposition of size-selected copper and silver nanoparticles (NPs) on polymers using cluster beam technique is studied. It is shown that ratio of particle embedment in the film can be controlled by simple thermal annealing. Combining electron beam lithography, cluster beam deposition, and heat treatment allows to form specific patterns (arrays) of metal NPs on polymer films. Plasticity and flexibility of polymer host and specific properties added by coinage metal NPs open a way for different applications of such composite materials, in particular, for the formation of plasmonic structures with required configurations which can be applied for wave-guiding, resonators, in sensor technologies, and surface enhanced Raman scattering.

INTRODUCTION

Light interaction with metal nanoparticles (NPs) gives rise to a number of fascinating optical phenomena. One of the directions of research is the search for configurations that utilize localized plasmon resonances and enable to amplify the local electromagnetic fields produced by NP assembling or forming specific spatial architectures. Therefore, there is a strong interest in the formation of NP arrays for practical applications in nanoscale optics, surface enhanced Raman spectroscopy, and optical sensing [1-4].

There are various possibilities to produce NP assemblies or arrays. For example, gluing of gold NPs by cucurbit[n]uril provides rigid interparticle separation [5]. In another approach, the NPs are chemically bound into grooves produced by lithography [2]. The bounding can be also achieved by modulating the spatial electrostatic potential [6]. There are approaches utilizing cluster beam deposition through stencil masks [7]. Most of the methods involve polymer materials either at intermediate production stages (for example, under lithography) or in final sample configuration because polymer materials as plastic and flexible hosts provide a number of practical advantages.

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Therefore, the behavior of metal NPs on polymer surfaces under different treatment regimes is also of high practical interest.

In the current paper, size-selected Cu and Ag NPs are deposited on the polymer films from cluster beams. NP behavior under thermal annealing is studied in order to control the degree of particle embedment in the films. By combining cluster deposition and electron beam lithography (EBL), designed patterns (arrays) of NPs are obtained showing a way towards the formation of plasmonic architectures with required configurations.

EXPERIMENTAL DETAILS

Copper and silver NPs are produced by means of gas aggregation in vacuum using a magnetron sputtering cluster apparatus (MaSCA). In the apparatus, a metal target of 99,99% purity is sputtered, clusters are formed, collimated into a beam, size-selected using an electrostatic quadrupole mass selector, and soft-landed on the samples. More details about MaSCA can be found elsewhere [8].

The first series of experiments is conducted to control the metal NPs embedment in the polymer films in order to improve the adhesion and make the soft-landed NPs resistant to wet chemical procedures [9]. For these investigations, a few samples with thin (50 nm) poly(methyl methacrylate) (PMMA) films are prepared by standard spin coating on Si substrates. Size-selected Cu NPs (about 15 nm in diameter) are deposited at low surface coverage in order to monitor individual clusters. The deposition is followed by thermal annealing at 125 °C (above glass-transition point of PMMA) in a few steps. The NP embedding is monitored by the atomic force microscopy (AFM) measurements imaging the same clusters after each annealing step.

To form arrays, the cluster beam deposition and EBL are combined. The substrates are covered by thin (100 nm) layer of photoresist (PMGI) followed by thin (also around 100 nm) PMMA layer using standard spin-coating. In these experiments, patterns representing stripes of different width with varying periodicity are exposed in PMMA by electron beam. To make the strips a few nm thick layer of gold is deposited by evaporation (otherwise PMMA is charged by the electron beam). After the exposure, the PMMA is developed in a solution of methyl isobutyl ketone and isopropanol (1:3 mixture ratio) for 60 s, thus, forming a periodic structure of linear trenches down to the photoresist layer. Size-selected copper (15 nm in diameter) and silver (18 nm in diameter) NPs are deposited in low-energy regime on the patterns reaching the coverage of a monolayer of NPs across the surface. After the deposition, the samples are annealed at 180 °C for 5 minutes to facilitate partial immersion of the deposited NPs into the polymer films. After that a standard lift-off is performed to remove the PMMA yielding the designed patterns of metal NPs slightly embedded into the photoresist layer. The entire procedure is schematically shown in figure 1.

The samples are studied by AFM in tapping mode utilizing Ntegra Aura nanolaboratory (from NT-MDT). Commercial cantilevers with sharp silicon tips (radius of curvature < 10 nm) are used. The extinction spectra are obtained from optical transmission measurements using a double beam Perkin Elmer High-Performance Lambda 1050 Spectrometer in standard configuration.

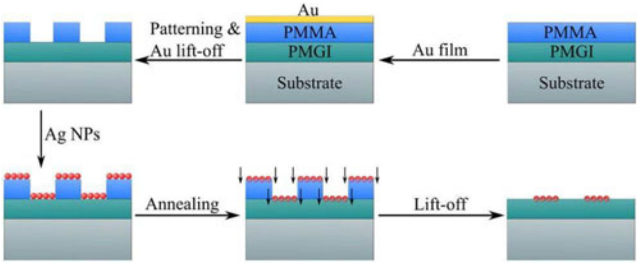

Figure 1. Schematic presentation of the protocol for the formation of NP arrays. See text for details.

RESULTS AND DISCUSSION

It is known from the earlier experiments that thermal treatment of polymer films with deposited metal NPs leads to their embedding into the bulk [8, 10, 11]. The driving force for the immersion is a large difference in surface free energy (surface tension) between metals and polymers. Annealing at temperatures in proximity to the glass transition point is required to increase mobility of polymer chains in the near surface layer, which allows the particle embedment between the chains.

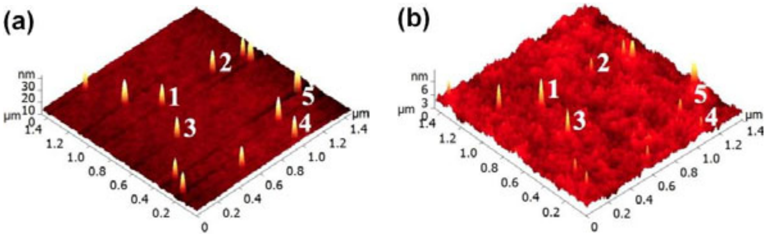

Figure 2. AFM images of (a) as deposited Cu NPs and (b) after 5 min of thermal annealing. One can monitor embedding of numbered NPs.

From a practical point of view it is very important to know the embedding dynamics in order to provide a defined degree of the NP immersion. Heights of as-deposited Cu NPs and the same ones after the several annealing stages are measured using AFM. The results are shown in figure 2 where one can monitor individual particles (numbered in the panels). It can be seen that the NPs do not diffuse on the surface (positions are not changed) but they undergo fast embedding (height is decreased) reaching about ¾ of diameter during first 5 min. Then, the immersion slows down and the annealing up to 60 min leads to further embedding for only 1-2 nm (images are not shown). In the current case, full embedment is not reached which can be caused by oxidation of copper NPs at elevated temperatures that changes surface tension and, therefore, the embedding dynamics. However, the oxidation hypothesis requires further investigation to be confirmed. The earlier experiments with Ag NPs showed that they can be fully embedded into PMMA. XPS studies did not show any oxidation of Ag NPs both after thermal annealing and after long-term storage in ambient atmosphere [12].

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Moreover, by a small variation of the annealing temperature around a glass transition point one can make the immersion a bit slower or faster. Thus, one can conclude that it is possible to tune the ratio of particle embedment by controlling the annealing temperature and time.

Cu NPs deposited on PMMA show an extinction band related to LSPR at around 590 nm. The first very short annealing causes a partial embedment of NPs in the polymer film and, thus, an increase of effective dielectric function of the surrounding medium leading to "red" shift of the plasmon band and higher band intensity (see figure 3(a)) as would be expected from the theory. However, more annealing steps in the ambient atmosphere lead to rapid quenching of the plasmon resonance. The most probable reason is bulk oxidation of the Cu NPs at elevated temperatures. The solution is found by the sample treatment in ozone for 30 min. that greatly enhances the stability of LSPR. As can be seen in figure 3(b) the ozonated samples withstand a few annealing steps and then show long-term stability of LSPR in ambient atmosphere. The main hypothesis behind the enhanced stability is that the ozonation leads to the formation of thin continues oxide shell around the metal core, thus, preserving it against further gradual oxidation and degradation of the plasmonic properties. However, more detailed study of this phenomenon is required.

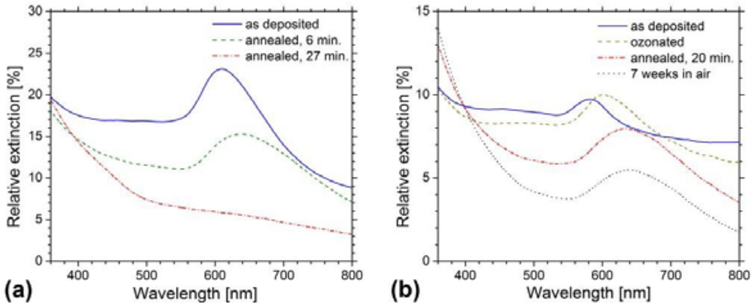

Figure 3. Spectra of relative extinction for (a) as-deposited Cu NPs followed by 1 min. annealing step and (b) as-deposited Cu NPs followed by ozone treatment, a few annealing steps (5 min. each), and 7 weeks keeping in ambient atmosphere.

Formation of ordered arrays is carried out for both copper and silver clusters. An example for the 250 nm wide stripes of Cu NPs on the photoresist is given in figure 4(a) demonstrating a successful realization of the suggested method combining EBL patterning and cluster beam deposition. For the Ag NPs, the width of stripes is reduced to 120 nm and the period is varied between 270-520 nm. The images in figures 4(b,c) show formation of almost single-particle rows for the case of silver. Further optimization of EBL and cluster deposition parameters can allow to reach a better quality of arrays. One can also approach more complex geometrical patterns.

Silver NPs are known to produce much stronger LSPR compared to copper ones with theoretically predicted value for the maximum at 360 nm in air [13]. Since our NPs are partly embedded into the photoresist, the plasmon band is slightly "red" shifted towards 400 nm as expected from the theoretical calculations [13] and can be seen in Fig. 5. If one compares the spectrum obtained from stripes with that measured on the sample with randomly deposited silver clusters (in both cases the deposition and annealing are carried out at the same conditions), an additional plasmonic band pronounced as a

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shoulder at λ ≈ 550 nm can be seen. It is believed that this band can be related to the coupling of dipole resonance of neighboring NPs similar to the case described in [12]. Further investigation of plasmonic properties is required in order to understand if periodicity of the patterns can lead to additional optical effects.

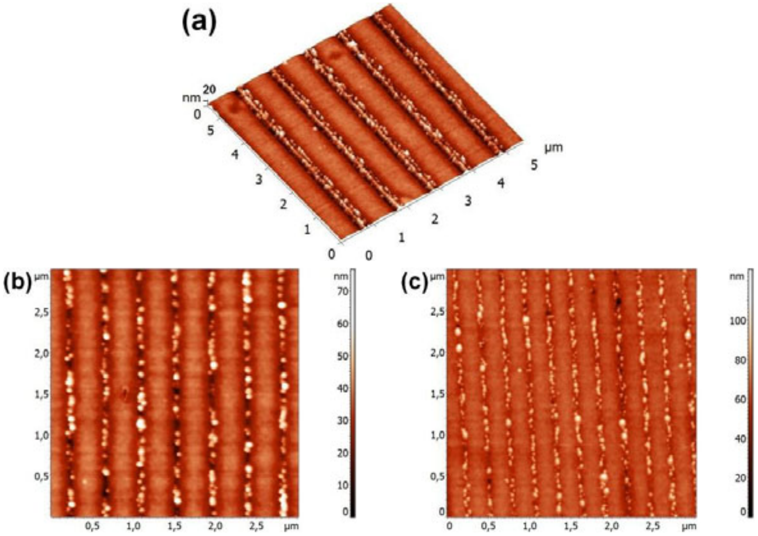

Figure 4. AFM images of stripes obtained by deposition of (a) Cu NPs (3D) and of Ag NPs with periods of (b) 420 nm and (c) 270 nm (2D).

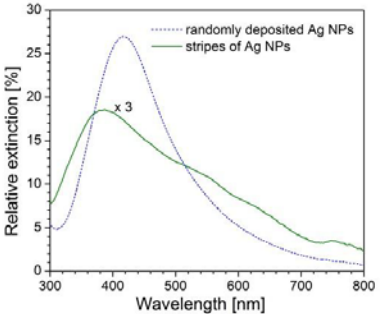

Figure 5. Spectra of relative extinction for randomly deposited Ag NPs and those organized in stripes.

CONCLUSIONS

Thin PMMA films with deposited size-selected silver and copper NPs are fabricated utilizing a cluster beam approach. It is found that the ratio of a particle

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embedment into the polymer film can be tuned by the post-deposition thermal annealing conditions, in particular, by varying the temperature and time. Together with control of cluster coverage by tuning the deposition time, the described approach represents an efficient method for the formation of polymer layers with controlled surface coverage or with controlled filling (after the annealing) of the metal NPs. Plasticity and flexibility of polymer host and specific properties added by NPs open a way for diverse applications. The current paper is focused on the plasmonic properties. Both types of NPs (copper and silver) deposited on the polymer films demonstrate characteristic plasmonic bands. Unfortunately, in the case of copper the annealing leads to damping of the plasmon resonance probably due to formation of copper compounds under ambient atmospheric conditions and elevated temperatures. The suggested solution is ozone treatment of the samples demonstrating a strong increase in stability of the plasmonic properties.

Combining lithography, cluster deposition and thermal annealing processes is found to be an effective approach in formation of the stripes composed of size-selected NPs By changing the lithography pattern the width and periodicity of the stripes can be varied. Generally, the patterns can be of different geometrical configurations required for practical cases. Thus, the suggested approach is a promising way for the formation of plasmonic architectures to be used in nanoscale optics, sensing, and SERS.

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