

POLYMER COMPOSITE FILMS WITH SIZE-SELECTED METAL NANOPARTICLES FABRICATED BY CLUSTER BEAM TECHNIQUE

Florian A. Ceynowa, Manohar Chirumamilla and Vladimir N. Popok
Aalborg University, 4A Skjernvej, 9210 Aalborg, Denmark, vp@nano.aau.dk

Formation of polymer films with size-selected silver and copper nanoparticles (NPs) is studied. Polymers are prepared by spin coating while NPs are fabricated and deposited utilizing a magnetron sputtering cluster apparatus. The particle embedding into the films is provided by thermal annealing after the deposition. The degree of immersion can be controlled by the annealing temperature and time. Together with control of cluster coverage the described approach represents an efficient method for the synthesis of thin polymer composite layers with either partially or fully embedded metal NPs. Combining electron beam lithography, cluster beam deposition and thermal annealing allows to form ordered 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 use of phenomenon of localized surface plasmon resonance (LSPR). Unfortunately, it is found that the thermal annealing used in the production process can lead to quenching of plasmonic properties in the case of copper. To solve this problem, it is suggested to treat the samples with ozone prior the annealing that helps to preserve LSPR by the quick formation of thin oxide shell protecting the metallic core against further gradual oxidation under the thermal treatment.

Introduction

Polymer films with partially or fully embedded metal NPs are of high interest for research and industry [1, 2]. For example, by controlling the filling factor of NPs in an organic matrix one can tune the mechanisms of the charge carrier transport from variable ranger hopping to percolation, thus, produce the composites with required conductive properties as well as with possibility to tune the conductance by stretching/contraction [3-5]. Another field of significant attraction is utilization of LSPR of noble metal NPs deposited on or embedded in a polymer [6]. This gives rise to application of polymer composites in sensor technologies [7, 8] and fabrication of plasmon resonators demonstrating enormous enhancement of quantum emitter's fluorescence [9, 10]. One more area of high practical interest is production of antibacterial coatings or components for medicine and food technologies in which polymers are used as cheap and easily formed material and metal or metal oxide NPs play bactericide role [11].

There are different approaches for the formation of metal/polymer composites among which are vapour phase deposition, wet chemistry, ion implantation and some others [12]. All these techniques have their advantages and disadvantages. In the current paper, we would like to address capabilities of the approach using cluster beams. The clusters are nucleated from a gas phase in vacuum, collimated in a beam and then steered towards a substrate for deposition or implantation. The advantages of this method are (i) in very good control of cluster composition due to the formation 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 as well as surface coverage or volume filling factor [13, 14]. Recently, it has been shown that the cluster beams can be used as an efficient method for embedment of metal NPs into polymers [15-17]. This approach provides capabilities for the formation of composite polymer films demonstrating optical and electrical properties attractive for practical applications [17-20].

In this work we are focusing on the study of particle immersion into polymer films and formation of ordered arrays of size-selected copper and silver NPs by combining cluster beam deposition and elec-

tron beam lithography (EBL). This approach brings great promises for the production of plasmonic structures with required configurations which can be applied for wave-guiding, resonators, in sensor technologies and surface enhanced Raman scattering (SERS).

Experimental

Polymer films are prepared by a standard spin coating procedure on quartz or silicon substrates. For the first series of experiments on controlled embedding of copper clusters, poly(methyl methacrylate) (PMMA) films of 50 nm in thickness are produced. For the formation of ordered arrays, a double layer structure with polymethylglutarimide (PMGI) at the bottom and PMMA at the top are fabricated. Both layers are 100 nm thick.

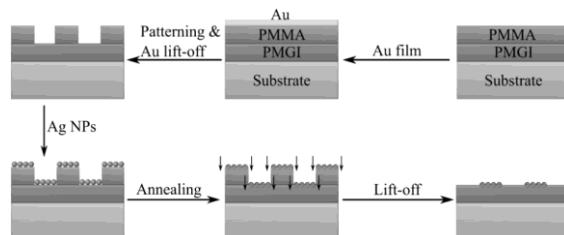


Fig. 1. Schematic picture of steps in preparation of ordered arrays of clusters

Metal clusters are produced and deposited on the substrates using magnetron sputtering cluster apparatus (MaSCA) [19]. Copper clusters are selected to be of 15 nm in diameter while silver ones of 18 nm for the current experiments. For the case of controlled embedding, the surface coverage by NPs is chosen to be low in order to monitor immersion of individual clusters into the polymer under the annealing using the marks made on the surface by a focused ion beam. For the formation of ordered arrays, the coverage is provided to be a monolayer of particles or more. Schematic drawing of the experimental steps involved into the preparation of samples in this case is shown in Fig. 1. It includes the spin coating of the polymer films, evaporation of thin gold layer for electron beam writing, formation of trenches in PMMA by the electron beam and removing gold,

cluster deposition across the entire surface and finally lift-off of PMMA in acetone.

The samples are studied by atomic force microscopy 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 transmission measurements using a double beam Perkin Elmer High-Performance Lambda 1050 Spectrometer in standard configuration.

Results and discussion

It is known from earlier experiments that thermal annealing leads to embedding of NPs into polymer bulk [16, 19, 21]. The driving force for this process is a large difference in surface free energy (surface tension) between metals and polymers. The annealing at temperatures close or above the glass transition point is required to increase mobility of polymer chains in the near surface layer, thus, providing a room for the particle immersion.

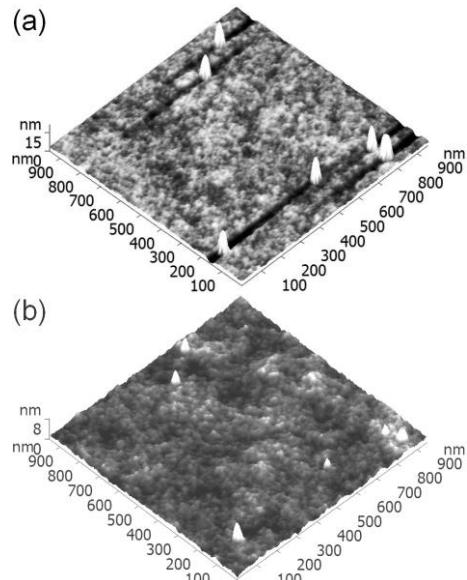


Fig. 2. AFM images of the same surface area with (a) as deposited NPs and (b) after the annealing for 5 min

To study time dependence of embedding, height of Cu NPs is measured before and after the annealing at 120°C using AFM. Making marks on the surface allows to monitor the immersion of particular NPs as can be seen in Fig. 2. It is observed that they do not diffuse on the surface and undergo fast embedding reaching about $\frac{1}{4}$ of diameter during first 5 min. Then the immersion slows down and the annealing up to 60 min leads to additional embedding for only 1-2 nm. In the current case, full embedment is not reached which is probably related to extensive oxidation of copper NPs at elevated temperatures that changes surface tension at the interfaces and, therefore, the embedding dynamics. However, in general one can conclude that it is easy to tune the degree of particle embedding by controlling the annealing temperature and time, which is very important way for practical use of NPs on polymers.

Formation of ordered arrays (stripes) is carried

out for both copper and silver clusters. An example of such stripes with width of 200 nm and period of 1 μm is shown for copper in Fig. 3. Unfortunately, the thermal annealing of samples, which is required to embed NPs into PMGI to withstand the lift-off, causes complete quenching of LSPR most probably due to bulk oxidation of the copper particles.

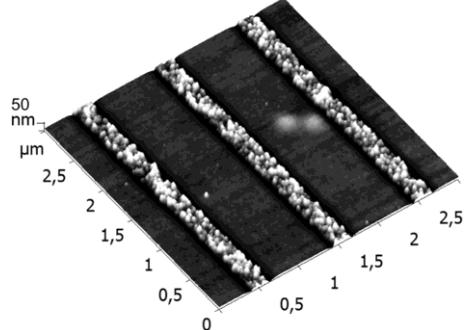


Fig. 3. AFM image of stripes formed by size-selected Cu clusters on PMGI

However, it is found that treatment of polymer films with copper NPs in ozone greatly helps to preserve LSPR. The ozonation leads to the formation of thin continuous oxide shell around the metallic core, thus, preserving the core against further gradual oxidation and degradation of the plasmonic properties. Small "red" shift of the band and increase of intensity after the ozone treatment (see Fig. 4) are in good agreement with the theory which predicts such changes due to an increase of dielectric function of the surrounding medium (formation of oxide shell). LSPR of this sample is found to be stable at ambient atmospheric conditions for the period over 1 month that confirms efficiency of the protective method. The small "red" shift of the band after the annealing compared to that after the ozone treatment is probably caused by some increase of the oxide shell thickness.

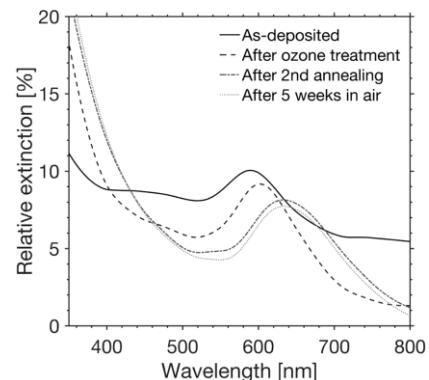


Fig. 4. Relative extinction vs wavelength for Cu NPs on polymer, treated with ozone, thermally annealed at 120°C for 10 min and after 5 weeks at ambient conditions. LSPR band is "red" shifted from original position at 580 nm and intensity is increased after the treatments

For the silver NPs, the width of stripes is reduced to approximately 100 nm and several substrates with different periods are fabricated. Fig. 5 shows AFM image of one of the arrays giving an impression that the stripes are mainly formed by single rows of NPs. 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 [22]. Since our NPs are partly embedded into PMGI, the plasmon band experiences a "red" shift towards 400 nm as can be seen in Fig. 6. If one compares the spectrum obtained from stripes with that measured on the sample with randomly deposited silver clusters, an additional plasmonic band pronounced as a shoulder at $\lambda \approx 550$ nm can be seen. It is believed that this band can be related to the coupling of dipole resonance of neighbouring NPs similar to the case described in [23].

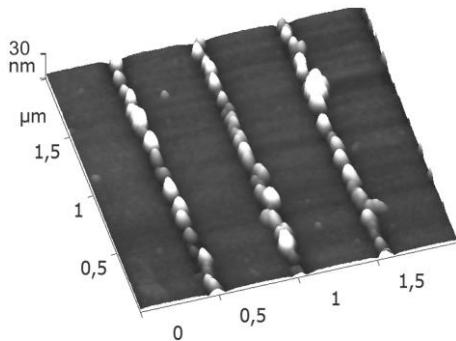


Fig. 5. AFM image of stripes formed by size-selected Ag clusters on PMGI

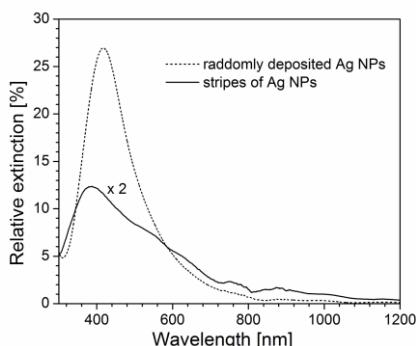


Fig. 6. Relative extinction vs wavelength for randomly deposited and ordered into stripes Ag NPs on PMGI

Conclusion

Thin PMMA films with embedded size-selected silver and copper NPs are fabricated utilizing a cluster beam approach. It is found that the degree of particle embedding into the polymer can be tuned by the conditions of the post-deposition thermal annealing, in particular, varying the temperature and time. Together with control of cluster coverage by changing the deposition time, the described approach represents an efficient method for the formation of thin polymer composite layers with controlled filling by the metal NPs. Plasticity and flexibility of polymer host and specific properties added by NPs open a way for different applications. In the current paper, the focus is put on LSPR.

Unfortunately, it is found that the annealing can lead to dumping of the plasmonic properties especially for highly-reactive metals such as copper due to formation of copper compounds under ambient atmospheric conditions and elevated temperatures. The suggested solution of this problem is a treatment of NPs in ozone leading to quick formation of oxide

shell protecting the metallic core from the following gradual degradation. This helps to preserve the plasmonic properties on long time scale at ambient conditions.

Second part of the paper describes an approach for the formation of ordered arrays of NPs combining cluster beam deposition with electron beam lithography. In particular, the stripes composed of size-selected metal NPs are successfully fabricated. By changing the lithography pattern the width and periodicity of the stripes can be varied. The obtained lined periodic structures are of interest for applications as gratings, resonators, waveguides, in SERS etc. Generally, the patterns can be of different geometrical configurations required for practical cases. Deeper study of optical properties of such arrays is required.

References

1. Faupel F., Zaporotchenko V., Strunskus T., Elbahri M. // Adv. Eng. Mater. 2010. – V. 12. – P. 1177.
2. Popok V.N. // Rev. Adv. Mater. Res. 2012. – V. 30. – P. 1.
3. Salvadori M.C., Cattani M., Teixeira F.S., Brown I.G. // Appl. Phys. Lett. 2008. V. 93. P. 073102.
4. Barborini E., Corbelli G., Bertolini G., Repetto P., Lecardi M., Vinati S., Milani P. // New J. Phys. 2010. V. 12. P. 073001.
5. Popok V.N., Lukashevich M.G., Lukashevich S.M., Khaibullin R.I., Bazarov V.V. // Surf. Sci. 2004. V. 566-568. P. 327.
6. Moores A., Goettmann F. // New J. Chem. 2006. V. 30. P. 1121.
7. Zeng S., Baillargeat D., Ho H.-P., Yong K.-T. // Chem. Soc. Rev. 2014. V. 43. P. 3426.
8. Willets K.A., Van Duyne R.P. // Annu. Rev. Phys. Chem. 2007. V. 58. P. 267.
9. Russel K.J., Liu T.-L., Cui S., Hu E.L. // Nature Phot. 2012. V. 6. P. 459.
10. Akselrod G.M., Argyropoulos C., Hoang T.B., Ciraci C., Fang C., Huang J., Smith D.R., Mikkelsen M.H. // Nature Phot. 2014. V. 8. P. 835.
11. Palza H. // Int. J. Mol. Sci. 2015. V. 16. P. 2099.
12. Prakash J., Pivin J.C., Swart H.C. // Adv. Colloid Interface Sci. 2015. V. 226. P. 187.
13. Binns C. // Surf. Sci. Rep. 2001. V. 44. P. 1.
14. Popok V.N., Barke I., Campbell E.E.B., Meiweis-Broer K.-H. // Surf. Sci. Rep. 2011. V. 66. P. 347.
15. Ghisleri C., Borghi F., Ravagnan L., Podesta A., Melis C., Colombo L., Milani P. // J. Phys. D : Appl. Phys. 2014. V. 47. P. 015301.
16. Hanif M., Juluri R.R., Chirumamilla M., Popok V.N. // J. Polym. Sci. B: Polym. Phys. 2016. V. 54. P. 1152.
17. Kuzminova A., Beranová J., Polonský O., Shelemin A., Kylian O., Choukrouv A., Slavinská D., Biederman H. // Surf. Coat. Technol. 2016. V. 294. P. 225.
18. Minnai M., Milani P. // Appl. Phys. Lett. 2015. V. 107. P. 073106.
19. Popok V.N., Hanif M., Ceynowa F.A., Fojan P. // Nucl. Instr. Meth. Phys. Res. B. 2017. (In press).
20. Hanif M., Juluri R.R., Fojan P., Popok V.N. // Biointerface Res. Appl. Chem. 2016. V. 6. P. 1564.
21. Ruffino F., Torrisi V., Marletta G., Grimaldi M.G., Appl. Phys. A. 2012. V. 107. P. 669.
22. Hanif M., Popok V.N., Mackova A., Miksova R. // J. Polym. Sci. B: Polym. Phys. 2015. V. 53. P. 664.
23. Novikov S., Popok V.N., Evlyukhin A.B., Hanif M., Morgan P., Fiutowski J., Beermann J., Rubahn H.-G., Bozhevolnyi S.I. // Langmuir. 2017. – in press.