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Ion-beam-induced formation of gold nanostructures on polymethyl methacrylate film

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Abstract. In this work, we study the behavior of a thin gold layer on the surface of a polymethyl methacrylate (PMMA) film under irradiation with keV atomic P and molecular PF_4 ions. Transformation of both the gold layer and the PMMA film depends on the kind of ions used. Formation of gold nanoparticles is found in all cases. This process is less efficient than in the case of the ion-beam-induced Au layer dewetting on SiO_2 substrate. The formation of nanostructured regions in the polymer bulk was also established. The dependence of transmission in the IR range on the stage of formation of nanostructures has been investigated. The PMMA matrix destruction is low as revealed by FTIR investigation. Obtained structures could be used as efficient substrates for surface enhanced Raman scattering studies.

Keywords: gold nanoparticles, irradiation with ions, polymethyl methacrylate, molecular effect, nanomaterials, polymer

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Ионно-индуцированное формирование наноструктур золота на пленке из полиметилметакрилата

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Аннотация. В настоящей работе исследуется поведение тонкого слоя золота на поверхности пленки полиметилметакрилата (ПММА) при облучении атомарными ионами P и молекулярными ионами PF_4 с энергиями порядка кэВ. Поведение как слоя золота, так и пленки ПММА зависит от типа используемых ионов. Формирование наночастиц золота происходит менее эффективно, чем при ионно-лучевом осушении слоя Au на подложке SiO_2. Установлено также образование наноструктурированных областей в объеме полимера. Выявлена зависимость пропускания в ИК-диапазоне от стадии формирования наноструктур. С помощью ИК-Фурье анализа доказано, что при формировании наноструктур полимер хоть и претерпевает изменения, но все же остается ПММА. Полученные структуры могут быть использованы в качестве подложек для исследований методом поверхностно-усиленного комбинационного рассеяния.

Ключевые слова: золотые наночастицы, облучение ионами, полиметилметакрилат, молекулярный эффект, наноматериалы, полимер

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Introduction

Nanocomposite materials are of widespread use in various fields from catalysis to sensing and more. Noble metal nanoparticles exhibit tuneable plasmon resonances over VIS-NIR spectral range. Incorporation of nanoparticles into a bulk matrix could increase hardness, wear resistance and other mechanical properties of a composite material. One can also tailor electrical conductivity, optical transmission and reflection, antimicrobial properties, temperature response, and many other characteristics. Noble metal, especially gold, nanoparticles have attracted attention, primarily due to their unique electronic, optical, thermal, chemical and biological properties, and, accordingly, promising potential applications in various fields, including biology and medicine, chemistry, photonics, materials science, and other interdisciplinary areas.

One of dry low-temperature techniques of gold nanoparticle synthesis is heating of a few nanometer thick gold layer [1], or its irradiation with accelerated ions [2]. This layer can be either deposited on a substrate, or buried ten to hundred nanometer deep. Moreover, metal ion implantation has been used to fabricate [3] and control the size, shape, and distribution [4-6] of metal nanoclusters in various matrices. In particular, carbon based polymer matrices are of interest due to possible biocompatibility of a composite [7]. Bombardment with small metallic clusters also can be successfully utilized to produce pinned or buried nanoparticles [8]. Besides a lot of efforts, there are still a number of unanswered questions; in particular, role of the relative density of collision cascades formed in the target by a fast ion during its stopping [9] is not clear. The influence of the substrate material on the process of particle formation can play a decisive role in the formation of nanoparticles. Local density of collision cascades formed by a stopping ion also affects radiation-related phenomena. Overlapping of collision sub-cascades formed by atomic constituents of a molecular ion gives rise to an increase in the density of the cumulative cascade formed by molecular ion. This fact let us study the effect of collision cascade density on formation of gold nanoparticles. This work is devoted to study change of a thin gold layer deposited on polymethylmethacrylate (PMMA) film under bombardment with accelerated molecular and monatomic ions.

Materials and Methods. Fabrication

Monocrystalline (100) *n*-silicon was used as a sample substrate. It was cleaned in hydrochloric acid, followed by thorough rinse with distilled water and acetone. Polymeric film was deposited

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by the drop-casting technique. 0,0104 g of polymethyl methacrylate was dissolved in 3,75 g of dichloroethane at 24° C. After that, 1 drop of solution was applied onto 1×1 cm^2 Si substrate. Samples were dried at room temperature for 24 hours. The thickness of the resulting PMMA films was about 250 nm, as measured by atomic force microscopy over iron needle applied scratch.

The gold deposition was carried out by vacuum thermal evaporation at a pressure of 10^{-5} Torr using an Oxford Instruments setup. The substrate was kept at room temperature during the deposition. Thickness of the gold layer on a test silicon sample (without polymethylmethacrylate) was measured by Rutherford backscattering technique using 0,7 MeV He^{++} ions (see [10] for detailes). Thickness of Au layer is 5,7 nm.

Finally, samples were irradiated at room temperature with P and PF4 ions using 500 keV HVEE implanter. Ion energies were kept as 1,3 keV/amu, which is equal to 40 and 140 keV for P and PF_4 ions respectively. Ion irradiation parameters are presented in Table I. The irradiation fluences used to compare the effect of irradiation were selected to keep constant number of displacements of gold atoms (displacements per atom) after bombardment with monatomic and molecular ions [9]. The values of DPA_{Au} were calculated from simulation data in the TRIM software package [11] as:

$$DPA_{Au} = nv \times D / n_{at},$$

where n_v is the average number of displacements of atoms per unit length produced by a single ion (cm^{-1}); is the concentration of atoms of a substance (for gold $n_{at} = 5{,}9\cdot10^{22}$ cm^{-3}); D is the fluence of incident ions (cm^{-2}). n_v was determined using the TRIM code simulation with the default values of threshold displacement energies in gold and PMMA layers. Number of displacements generated by a molecular ion was calculated as a sum of displacements produced by a one P and four F monatomic ions.

Table 1

List of irradiation parameters

Dose, DPA_{Au}	Fluence, cm^{-2}	
	P	PF_4
$0.27\cdot10^{-4}$	–	$4\cdot10^{10}$
$0.54\cdot10^{-4}$	$22.58\cdot10^{10}$	$8\cdot10^{10}$
$0.27\cdot10^{-3}$	$11.29\cdot10^{10}$	$4\cdot10^{11}$
$0.54\cdot10^{-3}$	$22.58\cdot10^{11}$	$8\cdot10^{11}$
$0.54\cdot10^{-2}$	$22.58\cdot10^{12}$	–
$0.27\cdot10^{-1}$	$11.29\cdot10^{13}$	$4\cdot10^{13}$
0.27	$11.29\cdot10^{14}$	$4\cdot10^{14}$
0.54	$22.58\cdot10^{14}$	$8\cdot10^{14}$
0.81	$33.87\cdot10^{14}$	$12\cdot10^{14}$

Most of the works related to the accumulation of damage in substances were carried out on crystal substrates [2], or SiO_2. The starting point for choosing the irradiation doses was the data from [7], where the results of PF_4 ion-beam – induced modification of a gold film on a silicon substrate are reported. The values of the irradiation doses used in this study and corresponding fluences are shown in the Table I.

Samples obtained were investigated by Fourier-Transform Infrared Spectroscopy (FTIR), atomic force microscopy (AFM) and scanning electron microscopy (SEM) after each irradiation step.

Results and Discussion

Figure 1 shows SEM and AFM images of a non-irradiated sample (Fig. 1, *a*, *d*) and samples irradiated with P ions (Fig. 1, *b*, *e*) and PF_4 ions (Fig. 1, *c*, *f*), at dose $DPA_{Au} = 0.81$. In the image with a non-irradiated sample, one can see that the formation of inhomogeneous nanosized regions occurs, in contrast to silicon, on which uniform Au layer is obtained at the given film thickness. It is also seen variable shape of gold islands and no single pattern describing the shape of these islands cannot be identified from the data obtained. Ion irradiation modify this surface with some notable trends. Indeed, gold structures become smaller and forrmation of bubble-like structures is seen. Fig. 2, *a* shows area covered by gold nanostructures, as deduced from SEM imagews. It is seen that gold occupied area decreases under ion irradiation. It follows from Fig. 2, *a* that same level of surface modification with P ions requires a higher dose compare to PF_4 molecular ions.

AFM images show that nanostructures are formed on the surface (Fig. 1, *a*, *b*, *c*). A significant part of these structures is seriously different from the images obtained by SEM (Fig. 1, *d*, *e*, *f*).

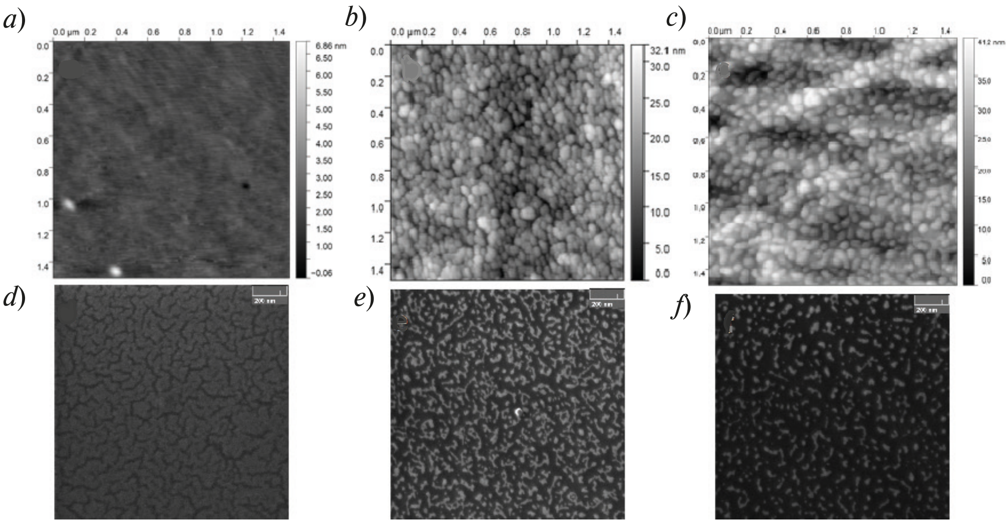

Fig. 1. SEM(*d*, e, *f*) and AFM(*a*, *b*, *c*) images of a non-irradiated sample (Fig. 1, *a*, *d*) and samples irradiated with P ions (Fig. 1, *b*, *e*) and PF_4 ions (Fig. 1 *c*, *f*), at dose DPA_{Au} = 0.81

There are two possible ways in which the difference may have arisen. Possibly, degradation of the polymer occurs under heavy ion irradiation and gases are released under the surface, which form gas nanobubbles, observed on AFM images. There is also a probability that in during gold deposition and ion irradiation, gold atoms diffuse into the polymer layer. These pattern will not be visible in SEM images due to the light molecular weight of PMMA.

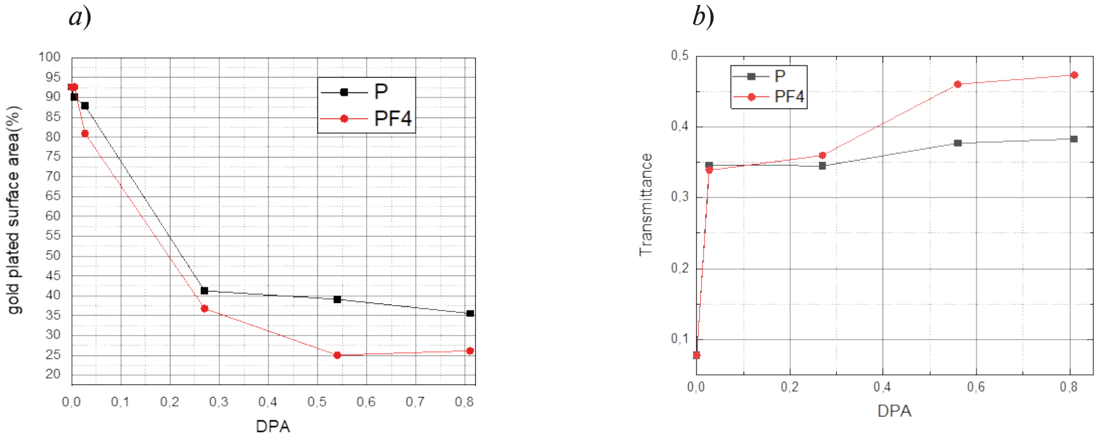

Fig. 2. Gold covered part of a surface as deduced from SEM (*a*) and IR transmission taken at 2000-2750 range (*b*) of irradiated samples as a function of ion dose

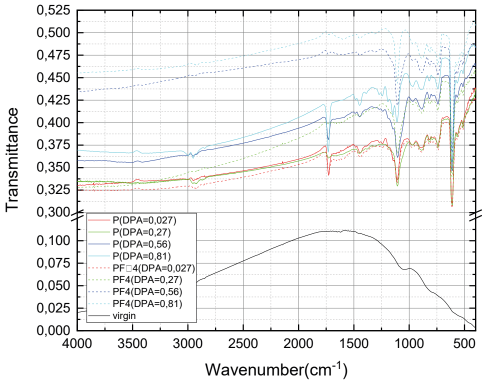

Fig. 3. FTIR spectra of samples: non-irradiated (black solid) and irradiated to various doses by P (solid colored) and PF_4 (dotted colored) ions

The transmission spectra in the IR spectral range taken from the samples are shown in the Fig.3. Several PMMA characteristic absorption peaks are visible at 2940cm^{-1}, 1725cm^{-1}, 1144cm^{-1}, 988 cm^{-1}. Overall transparency of the sample increases with the dose increase. Spectra of samples irradiated to highest doses used (DPA_{Au} = 0.81) confirm that the polymer has not been destroyed. The characteristic PMMA group vibrations are still clearly visible (Fig.3). Also, it is seen from Fig. 3 *a* and *b* that the transmitted light intensity correlates well with the surface area occupied by the metal nanostructures. This area depends on the level to which the metal layer was modified (or else, which dose the samples were irradiated to). Thus, due to the high speed of Fourier spectra collecting, this finding let us recommend FTIR as a useful technique for fast analysis of the stage of the process of nanoparticle synthesis by ion bombardment.

Conclusion

When applying a thin layer of gold on polymethyl methacrylate, nanostructures are formed on the surface, occupying almost the entire area. Irradiation with P and PF_4 ions makes it possible to modify nanostructures, while irradiation with PF_4 ions makes it possible to do this much more efficiently. In the process of modifying the gold layer, the PMMA substrate, although undergoing changes, is still not destroyed. It was also possible to observe the dependence of the transmission intensity in the IR range on the stage of formation of nanostructures, which makes it possible to use FTIR as a fast method for assessing the stage of formation of nanoparticles from thin metal layers on IR-transparent substrates. The formation of nanostructured regions in the polymer bulk was also established.

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