FORMATION OF A LARGE-AREA MONOLAYER OF POLYSTYRENE FILM VIA THE SPIN-COATING METHOD

by

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The self-assembly methods, an inexpensive and high throughput technique capable of producing nanostructure arrays, relies on the formation on a monolayer of self-assembled nanospheres. This paper reports on the formation of large-areas monolayer polystyrene particles 150 nm in diameter onto monocrystalline Si (100) substrates by using the spin-coating method. In this method, the quality of the deposited monolayer is determined by the balance between spinning and solvent evaporation, accounted by two different forces, the centrifugal force and viscous shearing force, and their interplay. The key process parameters which influence the deposition process and determine the properties of polystyrene monolayers such as the spinning rate, time and concentration of PS particles in the solution were studied. By varying the experimental conditions in different steps the films quality can be easily improved and the optimized experimental parameters were achieved. A homogenous and well-ordered PS monolayer with a high surface coverage of 94 % was formed on a large-area substrate of 1 cm ×1 cm at specific conditions of a 2000 rpm spinning rate, 2 wt. % polystyrene solution concentration and 210 s duration of the spinning process. We conclude that this method can be useful in a variety of applications since it offers a stable and controllable approach to the fabrication of monolayer polystyrene films on a large-scale.

Key words: self-assembly, monolayer, polystyrene particle, electron microscopy

INTRODUCTION

Recently there has been a growing interest in the formation of nanoparticles on thin films surfaces due to their wide applicability in various fields. Ideally these nanoparticles should be of equal size, densely packed and arranged in a regular lattice. In particular, nanomask formation by nanosphere lithography *i. e.*, the self-organized arrangement of small particles during the controlled drying of a colloidal suspension on a solid surface could be a very versatile and cost effective alternative to other techniques [1-5]. In this technique a hexagonally closed packed monolayer of colloidal, mostly spherical particles is formed on a surface and the open interstices in between three neighboring particles are used as mask openings [6]. A number of reports have been published on the successful formation of such masks from SiO_2, ZnS, polystyrene (PS), and other nanoparticles [7]. Homogeneous monolayers of polystyrene nanospheres are widely used in data storage devices, displays, and sensors [8, 9] and are of particular interest.

The most common approaches to self-assembly are based on the fact that when the solvent of a polystyrene suspension evaporates, convective flow transports polystyrene spheres from the bulk of the suspension and deposits them at the drying front – a contact line. Self-assembly of polystyrene nanoparticles depends on various factors, like particle size and shape, size distribution, the inter-particle interactions, surface charge density, nature and the dimensions of the external forces, substrate surface properties as well as the other environmental factors such as temperature and evaporation rate. There are a number of different methods for the formation of self-assembly layers, for example gravity sedimentation, electrophoretic deposition, solvent evaporation, the Langmuir-Blodgett technique, the air-water interfacial floating method, dip coating, spin-coating, and many others [10-17]. Among them, the spin-coating method is found to be very popular. In this technique, a solution of nanospheres is first deposited on the substrate, and the substrate is then acceler-

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ated rapidly to the chosen rotation rate. Liquid flows radially, owing to the action of the centrifugal force, and the excess is ejected off the edge of the substrate. The film continues to thin slowly and the final thinning of the film is then due solely to solvent evaporation. The uniformity of the film thickness results from the balance of two opposite main forces: the centrifugal and the viscous forces. While the principle of the spin-coating thin film technique is well documented in the literature, this method is commonly used for multilayers formation and very little is reported on the monolayer processing.

Here, we report on the formation of a large-scale monolayer of PS microspheres with high surface coverage on a monocrystalline silicon substrate by the spin-coating method. The influence of experimental parameters on the quality of the deposited monolayers, like spinning rate, time and concentration of PS particles in the solution was investigated and discussed. By varying the experimental parameters, the specific conditions were achieved and the high-surface coverage monolayers were deposited on the 1cm × 1 cm area of Si surfaces.

EXPERIMENT

The monocrystalline (100) *p*-type Si wafers were cut into 1 cm 1 cm pieces and treated by distilled water and ethanol and then dried by ambient airflow. This procedure was used to remove the surface contamination of the silicon wafer. After that, the ultrasonicated silicon substrates were immersed in the "Piranha" solution (with a volume ratio of H_2SO_4:H_2O_2 = 3:1) for 15 minutes to improve their hydrophilicity. Subsequently, they were rinsed in distilled water several times and dried gently by ambient air-flow. It is important to emphasize that the substrates were prepared just before the beginning of the deposition process.

After the above treatment, the wafer was placed on the spin-coater and allowed to spin under controlled conditions. We used the spin-coater Model P-6708D (Specialty Coating Systems, Indianapolis, Ind., USA) which operates in three stages with a maximum speed of 8000 rpm. For the formation of the self-assembled monolayer the polystyrene particles sizes of ~150 nm were used. In order to obtain a uniform monolayer, the colloidal dispersion should be used to ensure that the surface of the solid substrate will be completely covered by the PS spheres. For that reason, PS spheres were dispersed in a mixed solution of water and ethanol with the volume ratio of 1:1, and then a droplet of the polystyrene suspension (20 μl) was dropped on the substrates fixed on a spin- coater at atmospheric pressure. The various spin-coating preparative parameters: spinning rate (2000-8000 rpm), concentration of colloidal PS particles (2-10 wt. %) and duration of spin time (60-210 s) were varied in order to achieve a highly covered monolayer of close-packed thin films of PS particles. The homogeneity and morphology of the resultant films were examined by the field emission scanning electron microscope (Tescan, MIRA3 FEG) and by optical microscopy.

RESULTS AND DISCUSSION

Effect of the spin rate

An efficient spin-coating process was explored to obtain monolayer films with PS particles sizes of ~150 nm. In order to obtain a homogenous coating over a large area, the balance between the centrifugal force and viscous shear force in the spin process of PS suspension had to be achieved [18, 19]. The viscous shearing force is mainly related to the physical and chemical properties of the PS microparticles on the surface of the Si substrate and is a constant physical quantity. As the centrifugal force is proportional to the rotation speed, the rotation rate is an important parameter of spin-coating. To optimize the spin rate, a series of depositions with a 2.5 wt. % concentration of the PS solution, were performed. The spinning rates used were 2000, 4000, 6000, and 8000 rpm, while the duration of the spinning process was the same for all experiments and was kept at 80 s. In order to analyze the morphology of the films formed imaging by using scanning electron microscopy was performed. We found that the spinning rate is a crucial parameter in the films structure. The SEM micrographs for all four PS layers are presented in fig. 1. It can be seen that the layers are uniform over the whole area presented, with

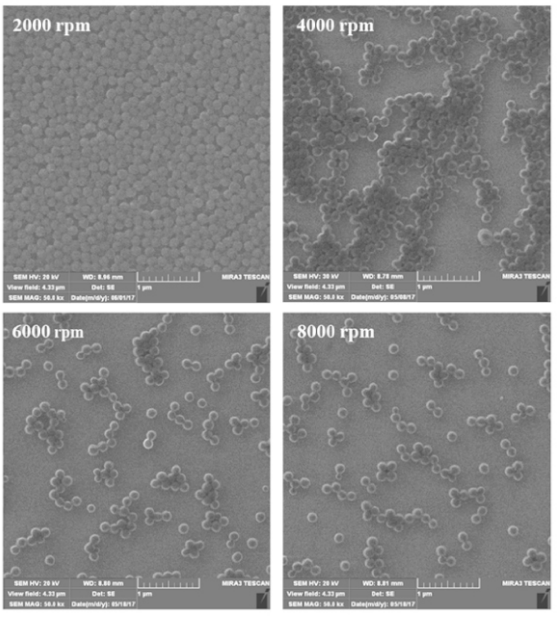

Figure 1. SEM micrographs of PS particles deposited on Si substrates at different spin rates: 2000. 4000, 6000, and 8000 rpm; concentration of PS particles in the solution was 2.5 wt. % and spinning time 80 s

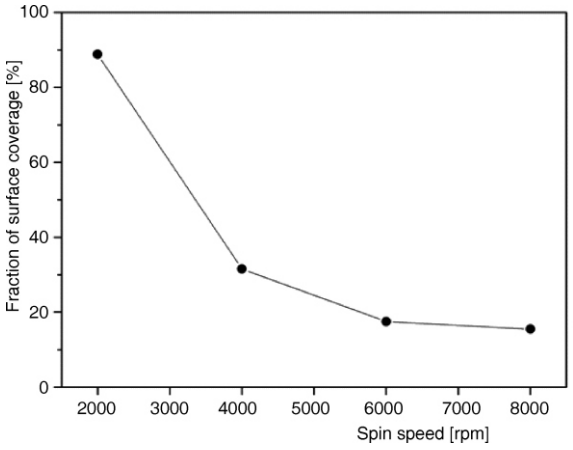

Figure 2. Relationship between the spin rate and fraction of surface coverage of the Si substrate

the PS spheres arranged next to each other. However, the layers are not continuous and some uncovered parts of the substrates were observed. In brief, different spin-coating rates results in different fractions of Si surface coverage.

The ratio of the substrate area covered by PS spheres for different spinning rates are determined and presented in fig. 2. In general, the fraction of surface coverage of the silicon substrate is negatively correlated to the spin rate. The maximum surface coverage is observed at 2000 rpm as compared to the higher spin rates, with ~90 % surface covered by PS spheres. When the spin rate exceeds 2000 rpm, the fraction of surface coverage rapidly decreases. From the results, the strong influence of the spinning rate on the solvent evaporation rate is confirmed and consequently on the monolayer formation of PS microspheres. Generally, in the spinning process the centrifugal force governs the main role causing flow of the solution toward the edge of the substrate. In the case of higher spinning rates (>2000 rpm), the strong generation of the centrifugal force evaporates the solvent very quickly. So, a large number of particles are expelled from the substrate forming the low-covered PS layers on the Si substrate. Considering the given results, in order to avoid the strong effect of the centrifugal forces, the low spin rate of 2000 rpm is taken as the optimal spinning rate for further investigations.

Effect of concentration of colloidal PS particles

In the fabrication of monolayers of particles by using the spin-coating process, the second parameter which strongly influences the quality of the films formed is the concentration of the PS suspension. Some previous investigations on the concentration dependence of the spinning process were performed and reported by Shinde *et al*. [20]. These authors developed layers of submicron size silica particles on a silicon substrate and they found that the monolayer surface coverage steeply increases with increasing the solution concentration. To evaluate the effect of the concentration of the dispersion solution of PS spheres on the monolayers structure on Si substrates PS films were produced at various concentrations of 2, 3, 4, 5, 7, and 10 wt. %, developed at a spinning rate value of 2000 rpm. Again, the spinning time was kept constant at a value of 80 s, the same as in previous depositions sets. For the evaluation of film quality different positions of the films surface were observed via SEM microscopy. The results of the analysis are presented in fig. 3. All six micrographs show that the prepared PS layers are uniform and continuous. In addition, the SEM images clearly demonstrate that in all six surface positions the PS particles are closely structured to form densely packed films.

The selected regions of the layers were further analyzed at higher magnification and the images are presented in the insets of the same figure. It is seen that in all cases the local microstructure of the layers is similar and they are densely packed. However, depending on the concentration of the solutions, various structures may exist, including monolayer films and transition regions separating various microstructures formed in multilayer structures. A typical monolayer,

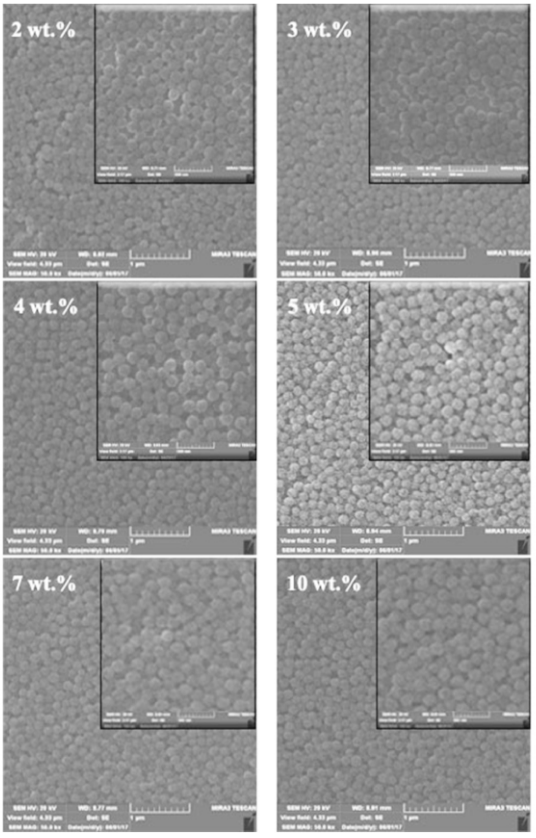

Figure 3. SEM micrographs of PS layers formed at various concentrations of PS particles in the solution: 2, 3, 4, 5, 7, and 10 wt. %; insets in the upper-right corner of each image show the micrographs at a high-magnification

where the substrate is almost fully covered by one layer of close-packed PS particles is obtained by deposition at concentrations of 2 wt. % and 3 wt. %. Depositions above these concentration values results in the formation of multilayer films. Depending on the values of concentrations the substrate is more or less covered by the second layer of PS spheres. This suggests that an identification of the optimal concentration is necessary in order to achieve a uniform PS monolayer film. In the case of ~150 nm PS particles and under the given conditions of process parameters of 2000 rpm of rotation rate and 80 s time of spinning, the lower solution concentrations of 2 wt. % or 3 wt. % are optimal.

Effect of spinning time

During the spin-coating process, the rotation speed and time should be large enough to disperse the PS solution across the full sample from the center to the edges. On the other hand, the evaporation rate must be small enough to avoid a breakdown of the droplet into several menisci, which can hinder close packing. One of the parameters which influence the rate of the solvent evaporation is the spinning time. So, another parameter which plays an important role in the process of films formation by the spin-coating method is the spinning time. Figure 4 shows the SEM images of PS particle layers obtained at 2000 rpm using a 2 wt. % polystyrene solution, at different values of spinning times of 60, 120, and 210 s. From the SEM images, it is seen that the surface coverage decreases with the increasing of the spinning time from 60 s to 120 s, and the PS sub-monolayer is formed, with the substrate coverage of ~71%. With further increase of the spinning time to 210 s the surface coverage again increases leading to the formation of a continuous monolayer. The surface coverage of the formed PS monolayer deposited at 210 s is about 94 %, which is very similar to the ~96 % coverage of the monolayer obtained at 60 s time of spinning. However, according to the enlarged sections of the images (given in the insets), we conclude that longer spinning time enhances better ordering of PS spheres during the monolayer growth. Obviously, the spinning time enhances the growth process solvent evaporation and leads to the rearrangement of PS spheres. So, to obtain a dense and well-ordered PS monolayer higher values of the spinning time are required. Similar observations of the layer ordering with the increasing of the spinning time were already recorded for the case of silica monolayers deposited on Si substrates [20].

As regards to the applicability of the PS monolayers the uniformity of the films on the large-scale order is required. For further examination of the quality of the PS film formed at the optimized conditions of the 2 wt. % solution concentration, the spinning rate of 2000 rpm and spinning time of 210 s,

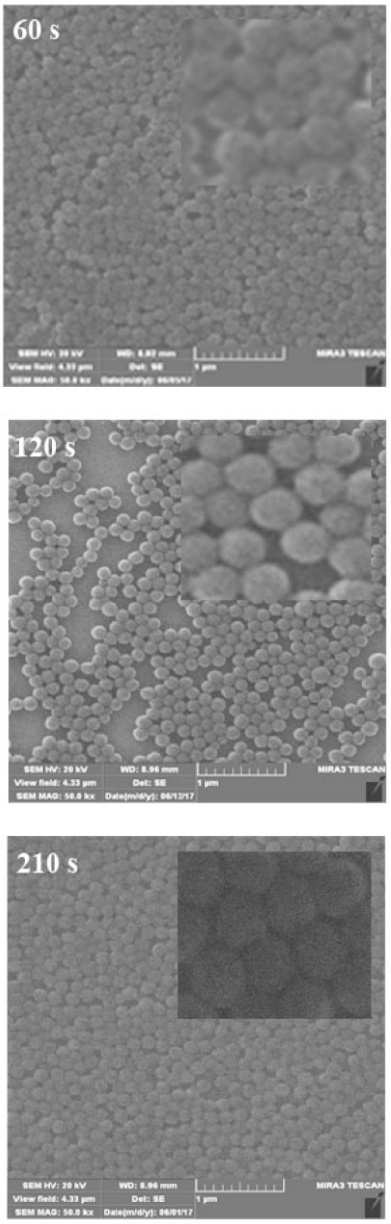

Figure 4. SEM micrographs of PS layers deposited on Si substrates at different spinning times: 60, 120 and 210 s, and constant spin rate of 2000 rpm and 2 wt. % concentration of the PS solution; insets present enlarged sections of the corresponding images

additional measurements were conducted. The photograph of the given layer obtained by the digital camera is presented in fig. 5(a). From the photo, one can obtain the overall view of the layer deposited on the 1 cm × 1 cm area of the Si substrate. A monolayer of PS assembled spheres from a concentrated PS suspension displays a nearly uniform color under the white light illumination, indicating the overall uniformity of the obtained monolayer colloidal crystal film. The film was further observed by optical microscopy imaging. Figure 5(b) and (c) shows two different areas of the films surface, as observed by optical microscopy. The first area was taken from the center of the sample, and the second was recorded from one of the edges of the

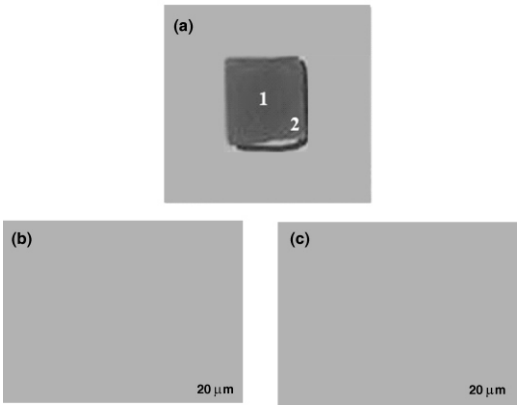

Figure 5. Photograph of the 1cm × 1 cm silicon substrate covered by a monolayer of PS spheres (a) and optical micrographs of two different areas (b and c) corresponding with those marked with labels 1 and 2 in (a)

film. The images from both areas show that the prepared colloidal crystal is uniform and homogenously covered by PS spheres. The overall results indicate that the spin-coating method is an effective for the formation of PS monolayers on the large-scale areas of the Si substrate.

CONCLUSIONS

The monolayers of PS particles of ~150 nm in diameter were successfully fabricated on 1 cm ×1 cm area Si substrates by using the spin-coating method. The influence of spin rate, time and concentration of PS particles in the solution on the properties of PS layers are studied in order to achieve the highest substrate coverage and uniform structures. The balance between spinning and the solvent evaporation rate is a crucial parameter in the developing of PS monolayers in a large areas. The highest surface coverage was achieved at 2000 rpm optimal conditions. The quality of the films was further improved by varying the spinning time and the concentration of the particles solution. The following optimized process parameters of 2 wt. % for the concentration solution and acceleration time of 210 s were found to be the best choice for surface coverage (~94 %) and layers homogeneity. We have demonstrated that the spin-coating technique is efficient among the other techniques for nanostructure self-assembling on the large-scale. The proposed method is a very fast and inexpensive way by which PS monolayers could be designed and has extensive application perspectives.

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AUTHORS` CONTRIBUTIONS

The main idea of applying a monolayer of self-assembled nanospheres onto Si substrates was put forward by Z. Lj. Rakočević and N. M. Bibić. The PS monolayers were prepared by A. H. Modrić-Šahbazović and I. M. Gazdić, while the analysis and discussion were carried out by V. R. Djokić, M. M. Novaković and A. H. Modrić-Šahbazović. The manuscript and figures were prepared by M. M. Novaković and were revised by N. M. Bibić and Z. Lj. Rakočević.

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ФОРМИРАЊЕ МОНОСЛОЈА ПОЛИСТИРЕНА НА ВЕЛИКИМ ПОВРШИНАМА СУПСТРАТА КОРИШЋЕЊЕМ МЕТОДЕ РОТИРАЈУЋЕГ ДИСКА

Методе самоуређења, које се заснивају на формирању монослојева самоуређујућих наносфера, представљају јефтину и веома заступљену технику за добијање уређених наноструктура. Овај рад извештава о формирању монослојева сфера полистирена пречника 150 nm, добијених на великим површинама монокристалних Si (100) подлога, коришћењем методе ротирајућег диска. У овом поступку, квалитет депонованог монослоја одређује равнотежу између брзине ротирања подлоге и испаравања растварача, односно, равнотежа између центрифугалне силе и силе трења, као и њихово узајамно дејство. Испитани су кључни параметри процеса који утичу на депозицију и одређују својства монослоја полистирена, као што су брзина ротирања, време ротирања и концентрација полистиренских сфера у раствору. Променом експерименталних услова у различитим степенима може се лако побољшати квалитет слојева, те су постигнути оптимални експериментални услови депозиције. Хомогени и добро уређени монослој полистирена, формиран са високим степеном покривености супстрата од 94 %, добијен је на великој површини подлоге од 1 cm 1 cm, при специфичним условима брзине ротирања од 2000 ротација по минути концентрације полистиренског раствора од два тежинска процента и 210 секунди трајања процеса. Показало се да ова метода може бити корисна у разним областима примене, јер нуди стабилан и контролисан приступ у производњи монослојних полистиренских филмова на нивоу великих површина.

Кључне речи: самоуређење, монослој, полистиренска сфера, електронска микроскопија