Physical and Chemical Changes of Polystyrene Nanospheres Irradiated with Laser

by Pratama Jujur Wibawa

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Physical and Chemical Changes of Polystyrene Nanospheres Irradiated with Laser

Mohd Ubaidillah Mustafa[a], Mohd Arif Agam[*b], Nor Rashidah Md Juremi[a], Farizan Mohamad[a], Pratama Jujur Wibawa[a], and Ahmad Hadi Ali[b]

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INTRODUCTION

Nanosphere lithography(NSL) is versatile hybrid bottom-up technique in fabrication nanostructure materials, that is facile, general in substrates or materials used, cheap and can be mass produce (parallel technique), is through a technique [5-10]. The technique was widely used and was endorsed by Richard Van Duyne group where NSL was found to be a very adaptable technique in producing nanomaterials, which have many potential applications such as catalysts, photonic materials and semiconductor devices [11-19].

Incorporating NSL with other complimentary techniques such as electron beam, heat treatment, chemical manipulation, and reactive ion etching [20] has shown the abilities to increase the versatility of NSL in producing either as mask patterning or fabrication nanoparticles on substrates surface. Thus combining NSL with other complimentary techniques can be categorized as the secondary lithography stage of NSL technique. The focused characteristic of these secondary lithographic stages for NSL is to be able to modify the nanopheres structure after they were let self-assembled on substrate surfaces.

One of the attempt at these secondary lithography stage of NSL is the over exposure of electron beam irradiation to polystyrene nanospheres, where, the electron beam is acting as manipulating agent. Experimental results have shown that, both the sizes and shapes of the nanospheres can be modified in a controlled manner depended on electron beam doses [20-21]. Modifying polystyrene nanospheres structure by electron beam irradiation has created a new lithography mask that otherwise is not available through self-assemble of the nanospheres alone. The mask created from irradiated and non-irradiated nanospheres can be used to precisely pattern periodic nanoparticle arrays.

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EXPERIMENTAL PROCEDURE

Single Layer Self-assembled Nanospheres

Silicon substrates were cut into 1 x 1 cm^2 in sizes from a silicon wafer and cleaned in acetone and dionized water for 1 hour each in an ultrasonic bath. The Silicon oxide (native oxide) were found to be hydrophobic surface, therefore assisting in the self-assembly of polystyrene nanospheres of 500 nm in diameter, purchased from Agar Scientific UK. Hexagonal close packed PSN arranged in single layer can be found easily on the substrate surface, beside double layer could be fabricated by repeating the process.

Preparation of Laser Exposure

LASER stands for Light Amplification by Stimulated Emission of Radiation. In our laser exposure we use commercially available Red helium neon (He Ne) laser, R-30025 Newport with minimum output of 1.5mW, producing red light with 633 nm wavelength.The experimental setup for irradiation of the nanospheres is shown as Fig. 1a, where the distance of about 51.5 cm between the laser and the substrate were chosen as the laser light covered almost 1x1 cm^2 of the substrate surface. The illumination intensity was not measured as we are focusing on the duration of laser exposure as manipulation parameter. The position of sample is perpendicular to the laser beam , where the entire surface area of the 1x1 cm^2 samples were exposed to laser irradiation as shown in Figure 1b. The light intensity of the laser modified the polystyrene nanospheres structures and have been confirm through FTIR.

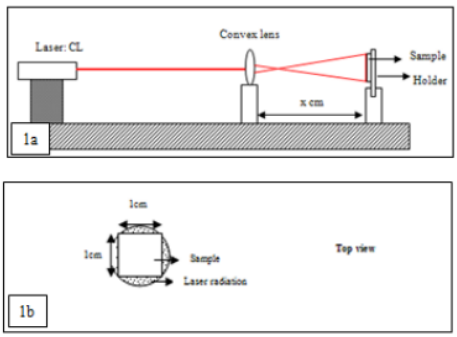

FIGURE 1. The experimental setup of irradiation into nanospheres.

Reactive Ion Etching Process: Ar-Oxygen Plasma Etching

Reactive ion etching (RIE) system manufactured by SnTEK Technology with couple capacitive plasma (ccp) is recently added to our facilities. These new facilities has been calibrated by manufacturer and we are focufsed on exposing the samples to Ar-Oxygen plasma. The same Ar-Oxygen plasma etching condition of Ar:O ratio of 2:1 sccm at 200 mTorr were used and the duration time were varied as different sizes of nanospheres (500 nm and 200 nm) will be etched differently as their trimness are corresponded to their initial sizes.

Chemical Analysis: FTIR Instrument

Fourier Transform Infrared spectrums were capture from Pelkin Elmer 101 which is used to detect chemical changes of irradiated nanospheres. FTIR data are arranged to give better ideas on the fabrication of nanodots, its chemical bondings and identifying elements in PSNs that contribute toward becoming more resistant to Ar-Oxygen Plasma treatment.

RESULT AND DISCUSSION

In Fig. 2, images of polystyrene expose to laser irradiation have shown no visible changes to the polystyrene nanospheres structure. Figure 2 (a) is an unexposed polystyrene nanospheres and Fig. 2 (b) is the irradiated polystyrene nanospheres. We assumed that there could be some changes to the irradiated polystyrene nanospheres as the photon of the lasers should have enough energy to somehow influence the polystyrene polymer chains, which directed us to used Ar-Oxygen plasma treatment to investigate the resistant behavior of the irradiated nanospheres.

Below is an example equation created with Word 97's Equation Editor. To move this equation, highlight the entire line, then use cut and paste to the new location. To use this as a template, select the entire line, then use copy and paste to place the equation in the new location.

Figure 3 (a-f) is the series of polystyrene nanospheres images exposed to different doses of laser bombardment and later etched with Ar-Oxygen plasma treatment. We have found that, under systematically laser irradiation exposure of duration of 10 minutes and with the same Ar-O plasma treatment, we are able to create carbonaceous periodic nanoparticle arrays.

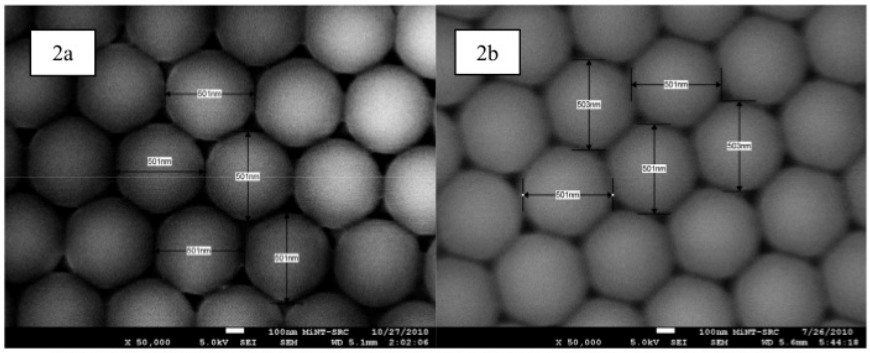

FIGURE 2. Before (2a) and after (2b) He Ne laser bombardment into polystyrene nanospheres.

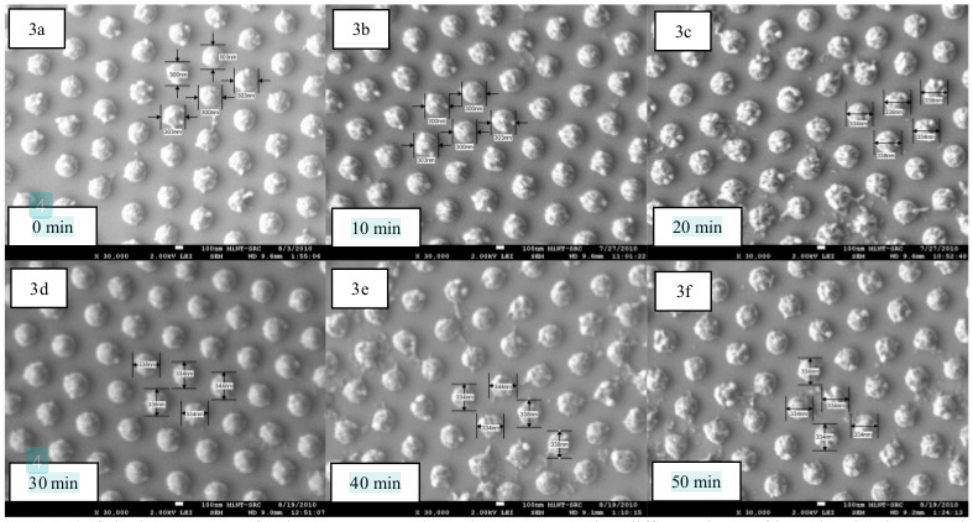

FIGURE 3. (a-f) is the sequence of polystyrene nanospheres images exposed to different doses of laser bombardment and later etched with Ar-Oxygen(ratio 2:1) plasma treatment. Average of PSNs diameter 5(a-f) (300nm;300nm;334nm;334nm; 334nm;334nm from their initial size of 500nm).

The Ar-O plasma treatment (ratio 2:1 sccm for 20s: for 500 nm diameter of PSNs) was used as a tool to prove that the chemical structure of the polystyrene polymer chains has been influence by laser irradiation. We assumed that if the polystyrene polymer chains are affected by the laser irradiation, there should be some characteristic differences of the irradiated polystyrene polymer if expose to reactive ion etching processes compared to the etching rate for ordinary PSNs.

The laser irradiation has somehow changes the nanospheres structure to become more resistant toward Ar-Oxygen plasma etching treatment. The original size of the PSNs are 500 nm in diameter and overexposure of laser irradiation and subsequence of Ar-Oxygen plasma treatment, the nanomaterials of 300-350 nm in sizes can be fabricated. The PSNs seem to react differently in various etching condition where the gases used are critical factors determining the etching rate of bare PSNs.

In Figure 2 a), the original nanospheres if etch by Ar-Oxygen plasma treatments were found to be etch to 300 nm diameters or shrunk to about 40% from its original size of 500 nm in diameter. Irradiated polystyrene images to different duration of laser irradiation and later etched with Ar-Oxygen plasma treatment.

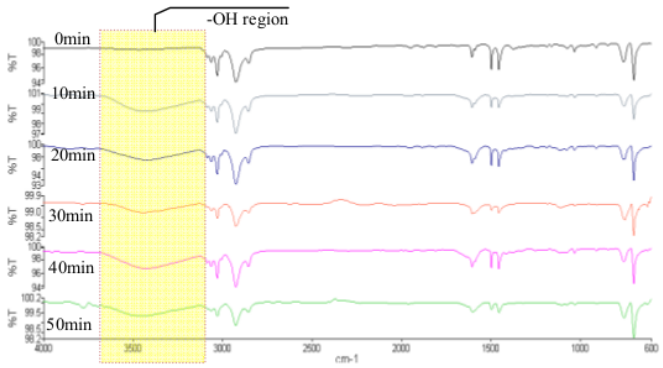

FIGURE 4. Chemical properties changes on duration of He Ne laser bombardment in FTIR spectrum analysis of transmittance.

TABLE 1: Position of the major IR band(cm^{-1}) of laser bombardment duration into polystyrene nanospheres.

0 min	10 min	20 min	30 min	40 min	50 min	Assignment
-	3410	3411	3410	3411	3411	-OH(broad)
3027	3027	3027	3027	3027	3027	nCH(ring)
2920	2921	2921	2921	2921	2921	nCH(CH_2)
1601	1601	1596	1596	1596	1596	nC=C(ring)
1493	1493	1493	1493	1493	1493	
1451	1451	1451	1451	1451	1451	d CH(CH_2)
753	752	752	752	752	752	g CH(5H)
696	695	695	695	695	695	g CH(CH_2)

FTIR spectrums have also showed some remarkable results, where the hydrogen element at the back bones could be released during laser irradiation, thus creating more densed carbonaceous nanoparticles as shown in figure 4. Table 1 shows the position of the major IR band(cm-1) of irradiated nanospheres and the assignment of each major IR band. If the Hydrogen in the back bone of the polymer chains or at benzene rings were taken away, the polystyrene were forced to create more carbonaceous or graphene-like structures and we are looking forward to prove it.

CONCLUSION

We have managed to show that over exposure of polystyrene nanospheres to laser beam irradiation could lead to polystyrene polymer structural changes, which become more resistant towards Ar-oxygen Plasma etching. They are turning from polymer toward carbonaceous or graphene like structures and could be used in many applications such as fabrication of nanopillars, emitters or toxic materials absorbance.

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PAGE 1

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