Preparation and Characterization of Silicon Dioxide Nanostructures by DC Reactive Closed-Field Unbalanced Magnetron Sputtering

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In this work, silicon dioxide nanostructures were prepared by a reactive closed-field unbalanced magnetron dc plasma sputtering technique. The target of p-type silicon was sputtered in presence of argon-oxygen gas mixture used for plasma generation and oxidation of silicon sputtered atoms. The x-ray diffraction patterns showed that only distinct peak corresponding to the crystal plane of (101) was observed with reasonable intensity. This is typical behavior of nanostructures. The scanning electron microscopy of the prepared samples showed that certain gas mixtures can produce the smallest particles with high probability for large grains to grow. Uniform distributed particles could be obtained using different mixtures. The energy-dispersive x-ray spectroscopy showed that only silicon and oxygen have appeared in the final sample with different weight percentages depending on the mixing ratio of the argon and oxygen gases. The SiO_2 prepared in this work are very good candidates to be employed in random gain media as scattering particles.

Keywords: Magnetron sputtering; Reactive sputtering; Silicon dioxide; Nanostructures
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1. Introduction

Due to its increasing uses in many new applications, especially optical, optoelectronics and electronics, synthesis and preparation of silicon dioxide were the goals of many research works and studies during the last two decades [1-5].

Silicon dioxide films are extensively used as low-index films in multilayer optical devices [6,7], passivated and/or protective layers of silicon devices [8], scratch resistant coatings for plastic ophthalmic lenses [9,10] and so on. Stoichiometry and stability of the films are important during applications. The usual methods employed for forming SiO_2 films involve oxidation of silicon at elevated temperatures (T>900°C) [11]. However, the high-temperature processing results in junction degradation [12].

There are many low-temperature methods used in the preparation of SiO_2 films, such as evaporation [13-15], pyrolytic decomposition [16], plasma enhanced chemical vapor deposition [17,18], reactive sputtering [19-21] and radio frequency (rf) magnetron sputtering [22]. Film composition as well as deposition and post-deposition processing conditions strongly affect film microstructure, and, consequently, many of its macroscopic properties [23-25].

This compound was prepared as thin films or powders by several different methods and techniques. The most common ones are sol-gel methods [26], the ball-milling technique [27], co-precipitation [28], electrospinning method [29], the hydrothermal method [30], the reverse micelles process [31], and the micro-emulsion method [32].

In this work, a reactive closed-field unbalanced magnetron dc plasma sputtering technique was used to sputter silicon target in presence of oxygen gas to prepare silicon dioxide (SiO_2) nanostructures at low pressures. The structural and optical properties of the prepared nanostructures are studied.

2. Experiment

The dc closed-field unbalanced magnetron (CFUBM) plasma sputtering system used in this work contains of a vacuum chamber, two discharge electrodes, vacuum pumps and accessories, and cooling and heating facilities. The chamber could be evacuated down to 10^{-3} mbar by a rotary pump and to 10^{-5} mbar by a diffusion pump. The base vacuum was determined by the purpose of the discharge process. Argon at maximum pressure of 0.8mbar was used as the discharge gas and its pressure was finely controlled by needle valve. Figure (1) show the schematic diagram of the dc plasma sputtering system used in this work. More details on this system can be found in references [33-35].

The inter-electrode distance could be easily varied from 0 to 10cm as the system was operated. The cathode was cooled down to about 10°C to prevent the secondary electron emission while the anode could be heated by an underneath heater or kept at room temperature. The target was p-type silicon wafer with 8cm diameter, 300μm thickness and 104 Ω.cm resistivity. The highly-pure oxygen was used as reactive gas. The mixture of highly-pure argon and oxygen gases was controlled by a gas mixing unit before entering the chamber. The gas mixture was flowing to the chamber throughout needle valve. The silicon wafer was placed on the cathode while the glass substrate on which the films were deposited was placed on the anode.

The film thickness was measured to be about 124nm for the sample prepared at 4cm inter-electrode distance, 0.5-0.8 mbar gas pressure, 2kV discharge voltage, 30mA discharge current and deposition time of 2 hours.

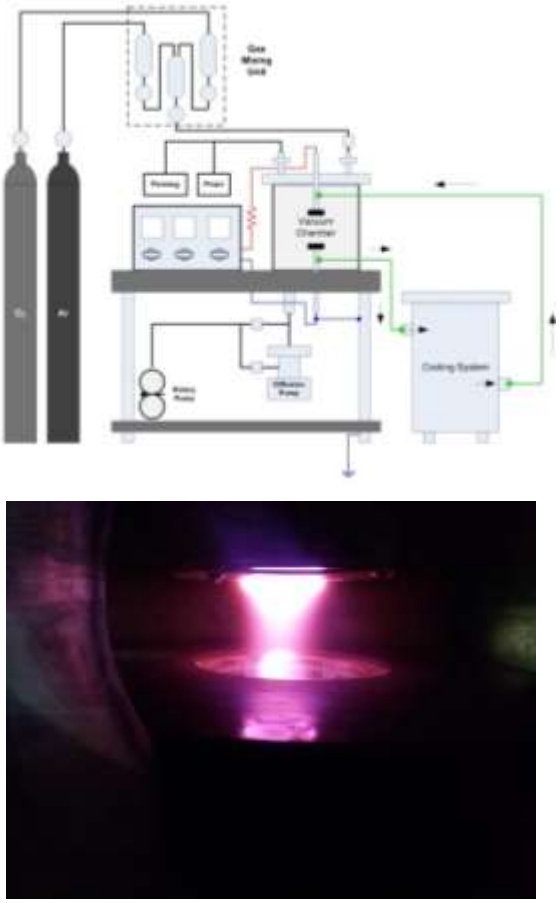


Fig. (1) (upper) schematic diagram of the CFUBM sputtering system used in this work and (lower) the plasma column generated by the discharge of argon

The characterization and measurements on the prepared samples included x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), atomic force microscopy (AFM), Fourier-transform infrared (FTIR) spectroscopy and UV-visible spectroscopy.

3. Results and Discussion

In the FTIR transmission spectrum of the prepared nanostructured SiO_2 thin film in Fig. (2), three distinct peaks are observed at 460.11, 805.08 and 1069.45cm^{-1}. They are attributed to the three different modes of vibration, bending, symmetric stretching and asymmetric, respectively, possessed by the silicon dioxide molecule. No peaks belonging to any other molecules in the final product were observed which reflects that plasma sputtering technique can produce highly pure structures.

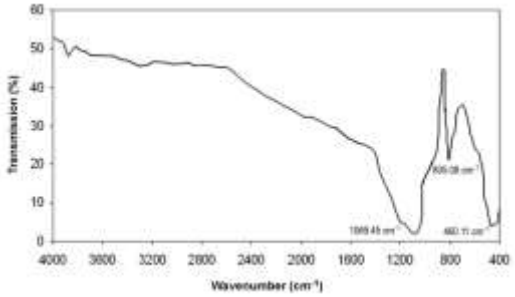


Fig. (2) The transmission FTIR spectrum of the prepared sample

Figure (3) shows the absorption spectrum of the prepared SiO_2 nanostructures in the UV and visible regions (200-800nm). High absorption is observed in UV region lower than 400nm. This absorption gradually decreases to reach it minimum in the range 500-800nm. Therefore, SiO_2 films are efficiently used as anti-reflection coatings in solar cells. This behavior of absorption encourages employing these nanostructures in random gain media as scatterers.

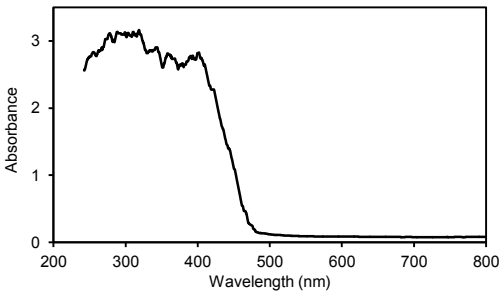


Fig. (3) The absorption spectrum of the prepared sample in the UV and visible regions (200-800nm)

Figure (4) shows the XRD patterns of the prepared SiO_2 nanostructures prepared in this work using different mixing ratios of argon and oxygen gases. The distinct peak observed at $2\theta=26.65°$ is attributed to the diffraction from (101) crystal plane. This assigns an inter-molecular distance of about 3.339Å, which is in good agreement to the standard value for SiO_2 (3.342Å). It is well-known observation that the diffraction of ex-ray radiation in nanostructures is different from that in the bulk form. Therefore, other featured peaks of x-ray

diffraction patterns in silicon dioxide nanostructured sample cannot easily recognized or observed.

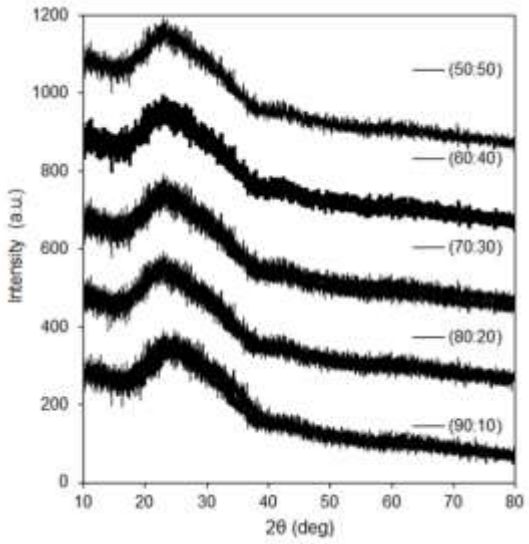


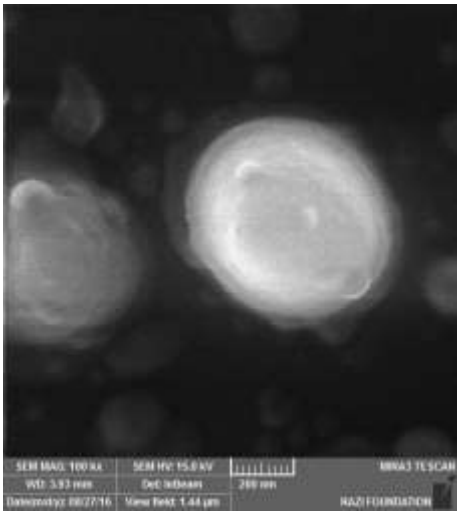
Fig. (4) The XRD patterns of the SiO_2 nanostructures prepared in this work using different mixing ratios of $Ar:O_2$ gases

Figure (5) shows the SEM images of the SiO_2 nanostructured samples prepared using different mixing ratios of $Ar:O_2$ gases. Samples prepared using ratios of 70:30 and 80:20 showed minimum values of SiO_2 nanoparticle sizes (25-30nm). However, the aggregation was apparently observed in both cases. On the other hand, reasonable homogeneity in the distribution of nanoparticles was observed in the sample prepared using ratio of 60:40.

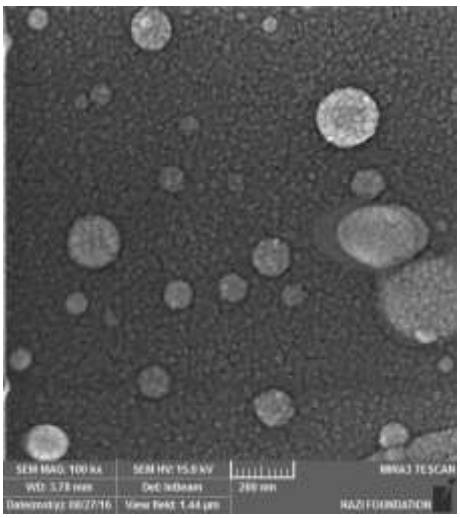
Figure (6) and Table (1) show the EDS results of the prepared samples using different mixing ratios of argon and oxygen gases. Decreasing the amount of oxygen in the initial gas mixture would lead to decrease the amount of oxygen in the content of the final sample (SiO_2). As well, the amount of silicon in the final product was increased with decreasing O_2 amount in the gas mixture. This can be ascribed to the fact that silicon atoms sputtered from the target did not find enough number of oxygen atoms to bond and form silicon dioxide molecules.

Table (1) The EDS results of the SiO_2 nanostructures prepared using different mixing ratios of $Ar:O_2$ gases

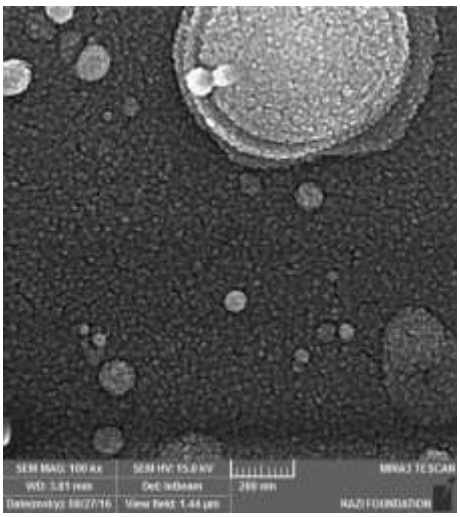
Sample	$Ar:O_2$	Si (wt.%)	O (wt.%)	O/Si
Z1	50:50	28.45	60.43	2.124
Z2	60:40	35.93	49.18	1.368
Z3	70:30	35.55	49.09	1.380
Z4	80:20	35.06	48.02	1.369
Z5	90:10	37.22	48.35	1.299



(a) (50:50)



(b) (60:40)



(c) (70:30)

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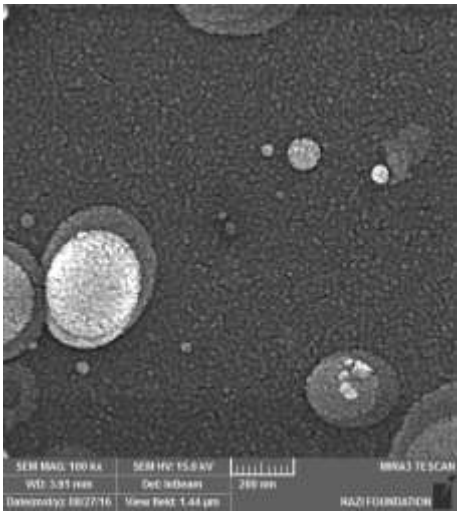
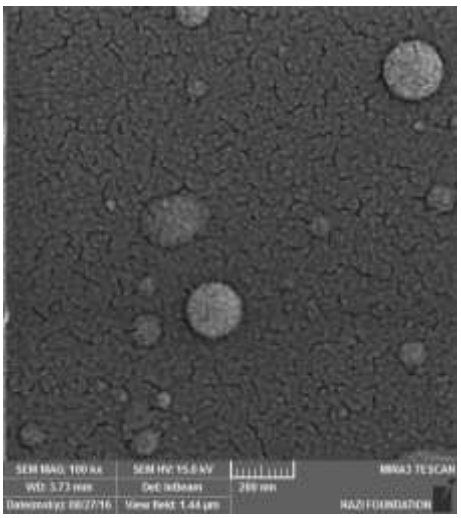


(d) (80:20)



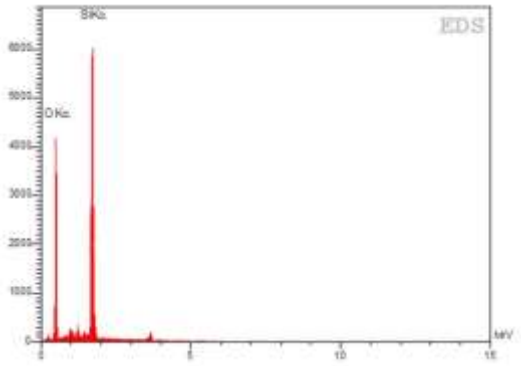
(e) (90:10)

Fig. (5) The SEM images of the SiO_2 nanostructures prepared in this work using different mixing ratios of $Ar:O_2$ gases

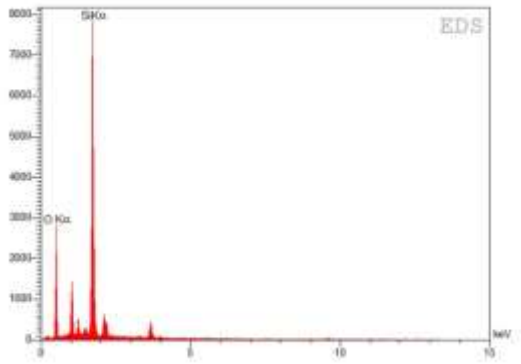
According to the correlation of SEM and EDS results, the growth of large grains (~400nm) seen in Fig. (5a) is attributed to the continuous formation of SiO_2 particles during the growth time as the statistical proportionality between Si and O atoms, i.e. two O atoms for each one Si atom, is perfectly satisfied. Decreasing the density of O atoms would decrease the number of SiO_2 nanoparticles over the available area, as shown in Fig. (5d and e), and hence the probability of large grains to grow is decreased too.

4. Conclusion

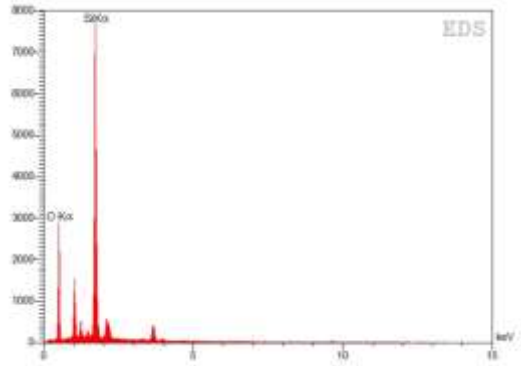
According to the obtained results, silicon dioxide nanostructures prepared in this work showed reasonably high structural purity as only one peak was observed on the XRD patterns while only silicon and oxygen were observed in the final sample according to the EDS results. Controlling the mixing ratios of $Ar:O_2$ gases before pumped into the deposition chamber is efficient tool to control the structural characteristics of the prepared SiO_2 samples.



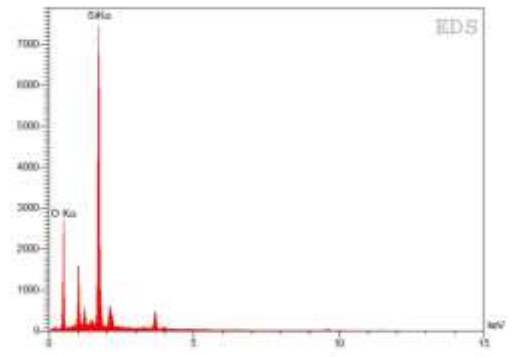
(a) 50:50



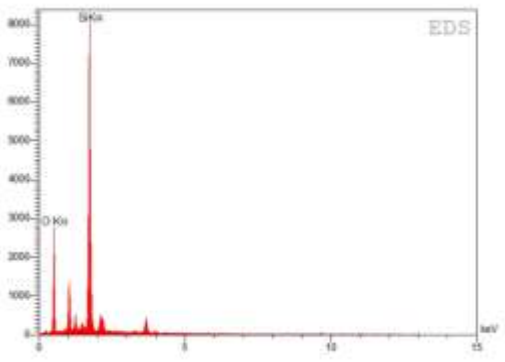
(b) 60:40



(c) 70:30



(d) 80:20



(e) 90:10

Fig. (6) The EDS charts of the SiO_2 nanostructures prepared in this work using different mixing ratios of Ar:O_2 gases

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