IRAQI JOURNAL OF MATERIALS
Volume (3) Issue (3) July-September 2024, pp. 25-32

Conjunctional Freezing-Assisted Ultrasonic Extraction of Silicon Dioxide Nanopowders from Thin Films Prepared by Physical Vapor Deposition Technique

Oday A. Hammadi

Department of Physics, College of Education, Al-Iraqia University, Baghdad, IRAQ

Abstract
In this work, the effects of different extraction parameters on the particle size of the nanopowders extracted from silicon dioxide thin film samples were studied. These nanopowders were obtained by the conjunctional freezing-assisted ultrasonic extraction method. Results showed that extraction parameters such as freezing temperature, ultrasonic frequency and application time are very effective in determining the nanoparticle size, which is very important for many applications and uses of highly-pure nanomaterials and nanostructures.

Keywords: Nanopowders; Nanoparticles; Physical vapor deposition; Silicon dioxide
Received: 11 March 2024; **Revised:** 12 June 2024; **Accepted:** 19 June 2024; **Published:** 1 July 2024

1. Introduction

For most thin film deposition methods and techniques, the extraction of thin film material represented a challenge to study the structural properties of this material without any possible interference from the material of the substrate on which such thin film was deposited. So far, scratching the film material from the substrate is the most common used method. However, in case of nonmetallic substrates, scratching cannot be controlled in order not to scratch their surfaces and hence some amount of substrate's material will exist in the final product even though this amount is very small. Precise measurements and characterization tests, such as x-ray fluorescence (XRF) and Fourier-transform infrared (FTIR) spectroscopy, energy-dispersive x-ray spectroscopy (EDX), can detect such small amounts of substrate's material. Therefore, structural purity of thin film material cannot be declared especially when such material is used for some applications requiring highly pure material.

Typical breakthroughs in spectroscopic and photonic applications are continuously satisfied when highly pure nanomaterials are employed. For example, quantum dot photonic devices (QDPDs) are critically sensitive to the presence of any material with the active nanomaterial [1-3]. Hence, the small contribution may result in a big effect on the device operation. Accordingly, measurements and characterization tests should be carried out with as much as possible guarantee that the prepared nanomaterial is highly pure [4].

Minimizing the probability of existing substrate's material in the extracted material makes any method or technique with such advantage most preferred in nanomaterials and nanotechnology. Unfortunately, mechanical methods cannot overcome this problem for accurate structural and spectroscopic applications [5]. Thermal methods are obviously avoided because the consequent increase in nanoparticle size is not desired at all [6]. Chemical methods are also avoided because they definitely include some reactions with tiny particles forming very large area (nanosurfaces) [7].

A recently invented method – known as conjunctional freezing-assisted ultrasonic extraction method – submits a highly efficient tool to get nanopowders from thin film samples without any probability to detect residual from substrate's material in the final product. However, the operation parameters of this method can reasonably affect the nanoparticle size. Therefore, further more typical jumps can be made in nanomaterials and nanotechnology as the nanoparticle size is sufficiently

controlled [8].

The principle of the conjunctional freezing-assisted ultrasonic extraction method can be shown in Fig. (1). The thin film layers are typically deposited on the substrate as shown in Fig. (1a) as each single layer may contain nanoparticles or molecules of the thin film material. Freezing of the prepared sample causes the nonmetallic substrate to shrink faster than the thin film and as soon as the temperature of the sample rises, the substrate again expands faster than the thin film. Therefore, their dimensions get different and the film surface is broken to form islands over the surface of the substrate. These islands keep adhered to the substrate surface at some points with loosen terminals, as shown in Fig. (1b). Strong vibration of these islands may soon extract large parts, as shown in Fig. (1c), while the weak vibration may extract smaller parts over relatively long time of application ultrasonic waves, as shown in Fig. (1d).

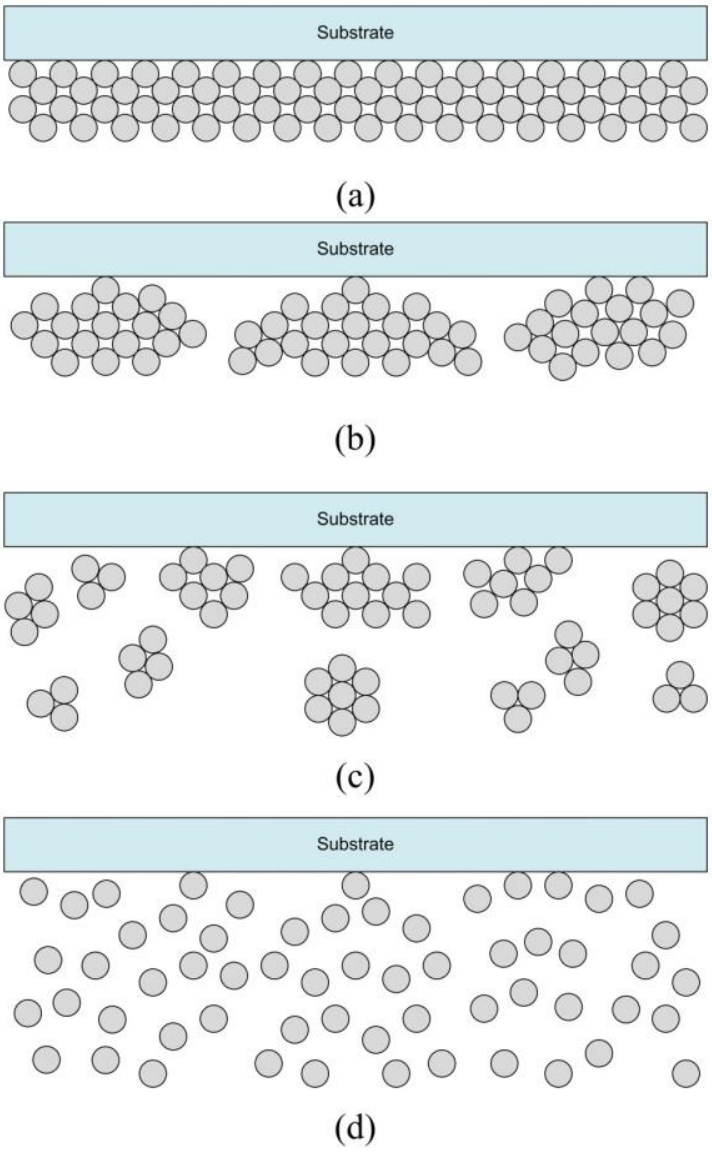

Fig. (1) Schematic representation of the conjunctional freezing-assisted ultrasonic extraction method

In this work, the effects of some operation parameters of conjunctional freezing-assisted ultrasonic extraction method, such as freezing temperature, ultrasonic frequency and application time, on the particle size of extracted nanopowders are studied.

2. Experimental Part

A homemade dc reactive sputtering system employing a closed-field unbalanced dual magnetrons (CFUBDM) assembly was used to deposit nanostructured thin films on nonmetallic substrates. This system was used to prepare thin films from several compound materials, such as nickel oxide (NiO), silicon nitride (Si_3N_4), silicon dioxide (SiO_2), and titanium dioxide (TiO_2) [9-13]. The operation parameters and preparation conditions of these samples were separately optimized. More details on the specifications and operation of this system can be found elsewhere [14-18].

Silicon wafer (p-type) was used as a sputter target to be maintained on the cathode of the discharge system. Argon gas is used to generate discharge plasma while the oxygen is used as reactive gas to form silicon dioxide molecules. The mixing ratio of argon and oxygen could be precisely controlled in a gas mixer before pumped into the deposition chamber. The discharge electrodes could be cooled using a cooling system employing water as a coolant. The crystalline phase of silicon dioxide nanostructures could be determined by controlling the operation parameters of magnetron sputtering system, especially gas mixing ratio, oxygen content in the gas mixture, and anode temperature. Optimum silicon dioxide nanostructures were prepared using $Ar:O_2$ gas mixture of 50:50.

As the deposition time is varied, the thickness of the prepared film is proportionally varied. Film thickness was measured by laser-fringes method. The nanopowder was extracted from thin film samples by the conjunctional freezing-assisted ultrasonic extraction method. Full description and specifications of this method can be introduced in reference [8]. The structural properties of the extracted nanopowders were determined by x-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM).

3. Results and Discussion

Figure (2) shows the XRD pattern of the silicon dioxide sample prepared using $Ar:O_2$ mixing ratio of 50:50. It is clearly observed that the prepared sample is amorphous, which is an indication to the formation of nanostructures. Consequently, no calculations of the structural parameters were performed as no specific peak could be analyzed.

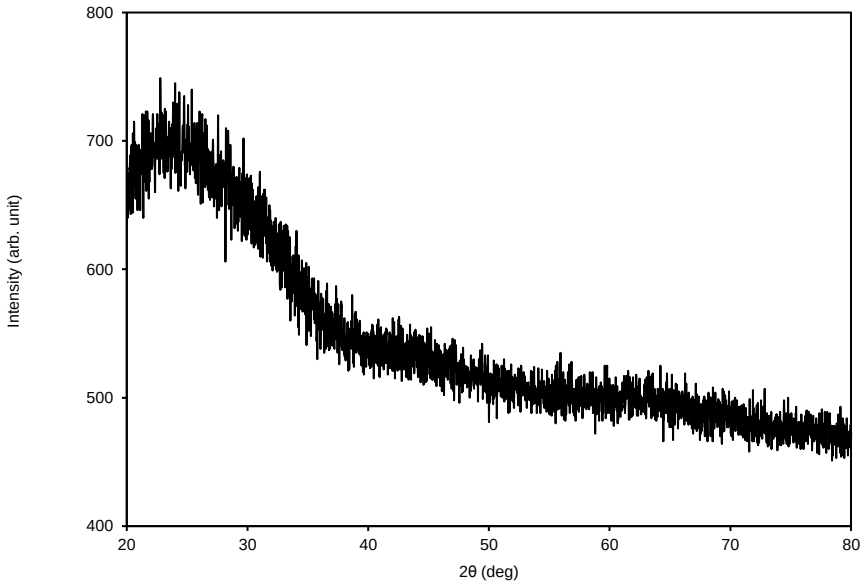

Fig. (2) XRD pattern of the optimum silicon dioxide sample prepared in this work

Figure (3) shows the SEM images of the optimum samples prepared in this work after four different deposition times. Film thickness is a function of deposition time, as it increases with increasing deposition time, therefore, the nanoparticle size can be considered as a function of film thickness.

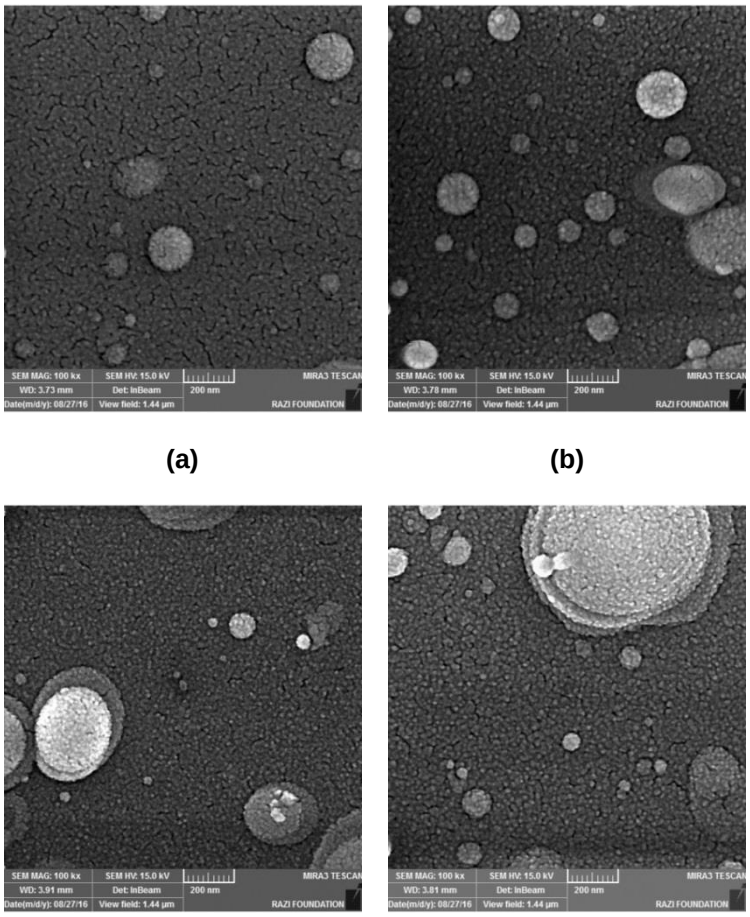

Fig. (3) SEM images of silicon dioxide nanostructures prepared in this work after deposition time of (a) 30 min, (b) 90 min, (c) 150 min, and (d) 210 min

It is clear that larger particles are grown after longer deposition times and aggregation is apparently observed in the samples prepared after deposition time of 90 minutes or longer.

Another observation from the SEM images is the spherical shape of SiO_2 nanoparticles. Such feature can be very important for certain applications those require uniform shape of nanoparticle in order to determine its size accurately as well as to assume that its reaction with electromagnetic wave, for example, is reasonably uniform.

Despite the further growth of nanoparticles larger than 200 nm, nanoparticles smaller than 50 nm can be seen all over the scanned area. This can be attributed to the nature of thin film growth and the passivation of thermodynamic effects among nanoparticles with relatively big differences in size.

Figure (4) shows the EDS of the sample prepared after deposition time of 30 minutes and the structural purity is apparent as no peaks belonging to elements other than silicon and oxygen are observed. Such structural purity is highly required in many applications especially those depend on the response of SiO_2 only to the applied effect (spectroscopic, electric, magnetic, etc.).

The stoichiometry of the formed compound (SiO_2) was confirmed for all samples prepared using different mixing ratios of Ar and O_2 gases in the gas mixture as the relative contents of silicon and oxygen in the final sample (Si/O) lie within the range 0.487-0.595 as shown in the table (1). The deviation from the ideal value (0.5) is about ±5.9%, which very small with respect to many operation and preparation parameters included in reactive sputtering technique.

Figure (5) shows the variation of nanoparticle size of the samples prepared in this work with the deposition time, which determines film thickness. As the deposition time is increased, the film thickness is approximately linearly increased and hence the layers of the thin film are further grown. This growth results the grains to get larger as observed in this figure. This behavior may turn to rapid increase in particle size for deposition times longer than 210 min as the bulk nature may dominate at higher values of thickness and hence the growth rate becomes reasonably higher to exceed the limit of 100 nm for nanoparticles.

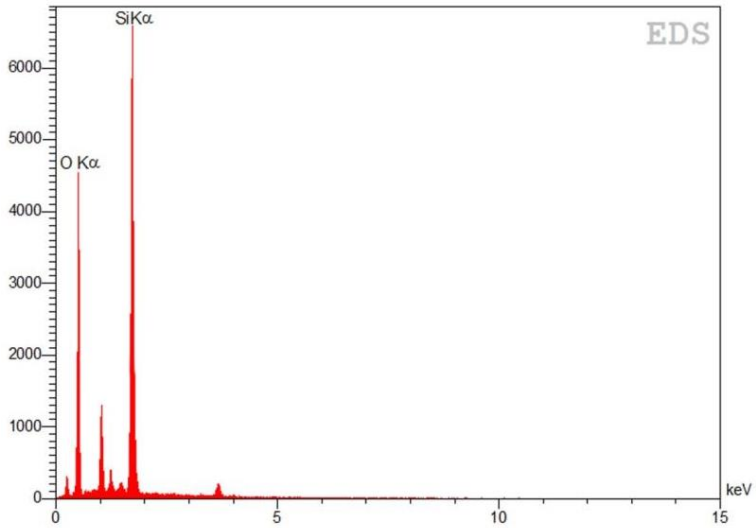

Fig. (4) EDS spectrum of silicon dioxide nanostructures prepared in this work after deposition time of 30 min

Table (1) Weight percentage contents of silicon and oxygen in the final product obtained from EDS results for the samples prepared using different mixing ratios of Ar:O_2 gases

Ar:O_2 ratio	Si (wt.%)	O (wt.%)	Si/O
50:50	29.45	60.43	0.487
60:40	30.19	59.88	0.504
70:30	31.03	58.84	0.527
80:20	32.45	57.91	0.560
90:10	33.94	57.08	0.595

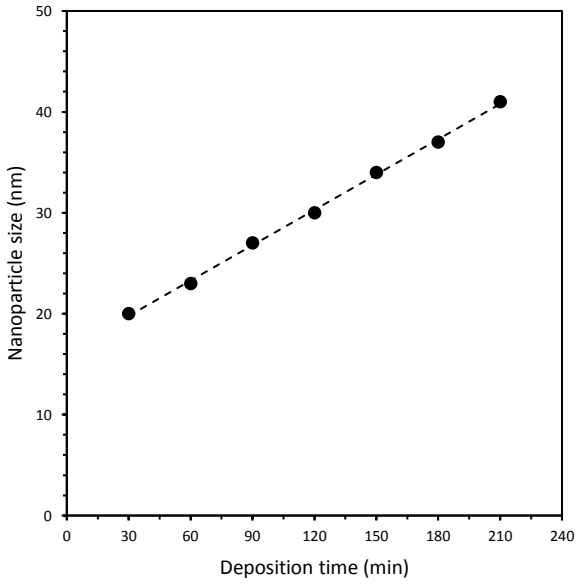

Fig. (5) Variation of nanoparticle size with deposition time for the silicon dioxide nanostructures prepared in this work

As the nanopowders were extracted from the thin film samples using the conjunctional freezing-assisted ultrasonic extraction method, the effect of freezing temperature on the value of ultrasonic frequency at which the nanopowder was completely extracted is shown in Fig. (6). As the freezing temperature is decreased, lower frequency is required to extract the nanopowder because lower freezing temperature lead to larger difference in shrinkage between the metallic layer and nonmetallic substrate. Hence, the adhesion of the film to the substrate gets lower and the ultrasonic frequency required to extract the film particles is accordingly lowered.

The variation of nanoparticle size with the ultrasonic frequency at which the nanopowder was extracted for the silicon dioxide structures prepared in this work is shown in Fig. (7). As the thin film is typically composed of at least several layers of silicon dioxide particles, higher ultrasonic frequency can vibrate atoms in different layers and hence extract larger particles.

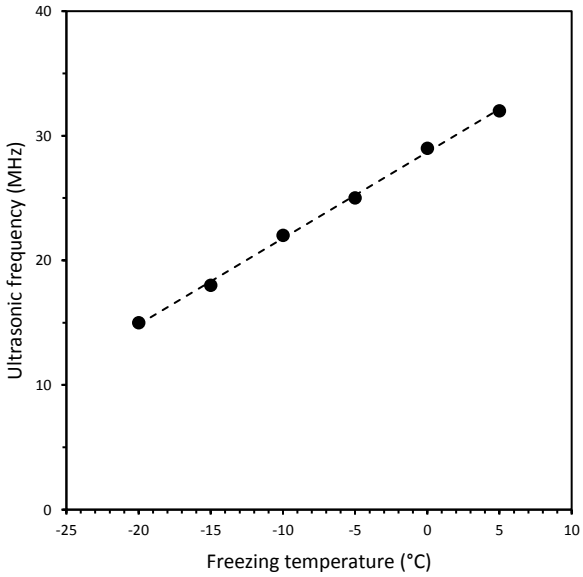

Fig. (6) Variation of ultrasonic frequency with freezing temperature for the silicon dioxide nanostructures prepared in this work

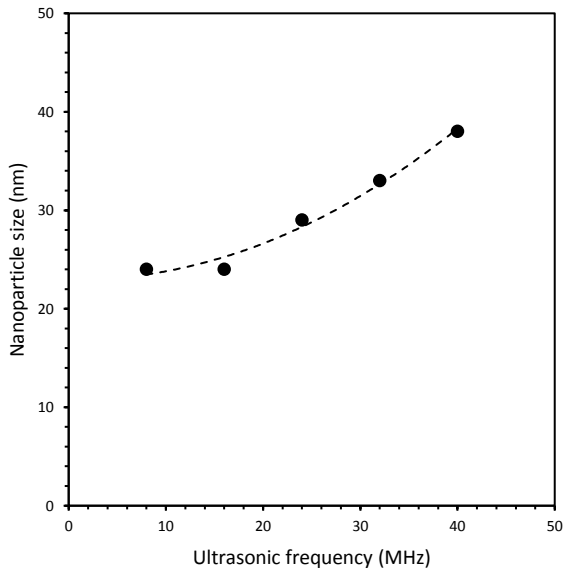

Fig. (7) Variation of nanoparticle size with the ultrasonic frequency for the silicon dioxide nanostructures prepared in this work

The time taken to apply the ultrasonic waves to the thin films sample before the extraction of nanopowder was completed is an effective parameter. Accordingly, the variation of nanoparticle size with application time at frequency of 32 MHz is shown in Fig. (8) for the silicon dioxide thin films. It is clearly observed that the particle size of the extracted nanopowder does not show large differences for application times from 30 to 210 minutes. This is attributed to the fact that particles of certain size are extracted by ultrasonic waves of given frequency regardless the application time. Extraction of particles containing molecules from different layers within the thin film is carried out at certain range of sizes as a function of ultrasonic frequency.

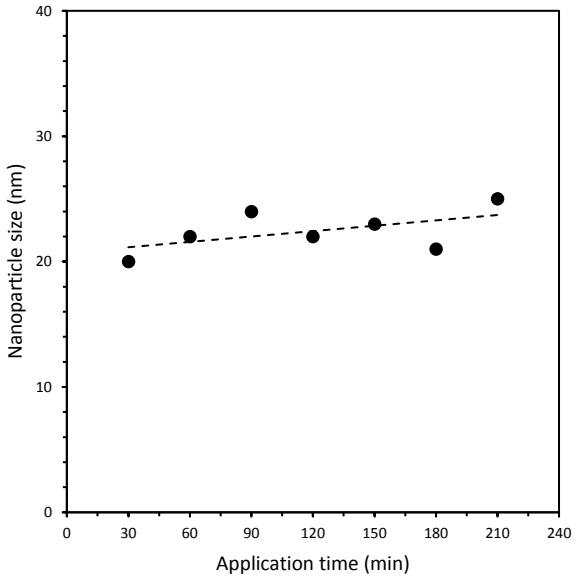

Fig. (8) Variation of nanoparticle size with the application time of ultrasonic waves for the silicon dioxide nanostructures prepared in this work

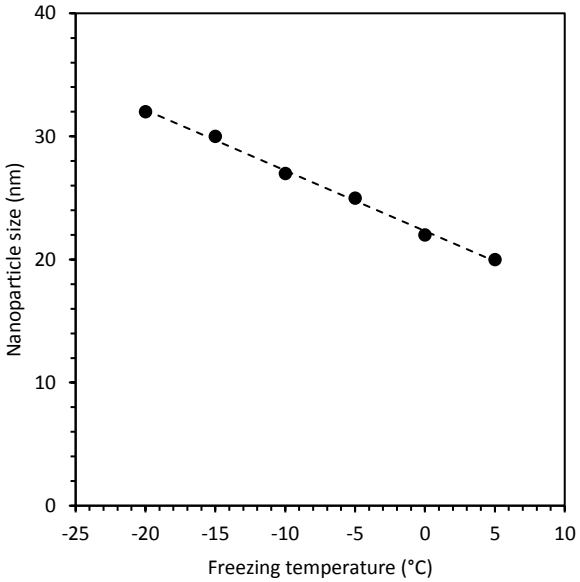

Fig. (9) Variation of nanoparticle size with the freezing temperature for the silicon dioxide nanostructures prepared in this work

As the extraction method mainly depends on the freezing stage, the freezing temperature may be very effective in determining the particle size of the extracted nanopowder. Figure (9) shows the

variation of nanoparticle size with freezing temperature for the silicon dioxide samples prepared in this work. It was mentioned before that the lower freezing temperature leads to larger shrinkage in the substrate on which the thin film is deposited and hence the adhesion between the film and the substrate gets lower and the film surface breaks earlier at the same value of ultrasonic frequency. Accordingly, larger particles can be extracted from the thin film before partitioning into smaller ones. In contrast, freezing to relatively higher temperatures leads to smaller shrinkage in the substrate and the adhesion between the film and the substrate gets higher. Therefore, the application of ultrasonic waves can extract silicon dioxide particles from the upper surface layer of the thin film, which means smaller particles. Layer-by-layer extraction at higher freezing temperatures produces smaller nanoparticles when compared to the case of lower temperatures.

4. Conclusion

As conclusions, freezing temperature, ultrasonic frequency and the time taken to apply ultrasonic waves on nanostructured thin films deposited on nonmetallic substrates are very effective to determine the nanoparticle size of nanopowders extracted from these thin film samples. The conjunctional freezing-assisted ultrasonic extraction method can be successfully used to extract highly-pure nanoparticles with approximately the same size of nanoparticles in the thin films deposited by physical vapor deposition methods and techniques. This technique is reliable, efficient and low cost to produce highly-pure nanomaterials with as low as possible particle sizes.

References

[1] S. Shen et al., “Titanium dioxide nanostructures for photoelectrochemical applications”, Prog. In Mater. Sci., 98 (2018) 299-385.

[2] E.A. Al-Oubidy and F.J. Kadhim, “Photocatalytic activity of anatase titanium dioxide nanostructures prepared by reactive magnetron sputtering technique”, Opt. Quantum Electron., 51(1) (2019) 23.

[3] K. Vidhya et al., “Structural and optical characterization of pure and starch-capped ZnO quantum dots and their photocatalytic activity”, Appl. Nanosci., 5 (2015) 235-243.

[4] K. Kim et al., “Towards visible light hydrogen generation: quantum dot-sensitization via efficient light harvesting of hybrid-TiO_2”, Sci. Rep., 3 (2013) 1-8.

[5] D. Wu et al., “Anatase TiO_2 hierarchical structures composed of ultra-thin nano-sheets exposing high percentage {001} facets and their application in quantum-dot sensitized solar cells”, J. Alloys Compd., 624 (2015) 94-99.

[6] H.A. Alhadrami et al., “Antibacterial Applications of Anatase TiO_2 Nanoparticle”, Am. J. Nanomater., 5(1) (2017) 31-42.

[7] M.T. Noman, M.A. Ashraf and A. Ali, “Synthesis and applications of nano-TiO_2: a review”, Environ. Sci. Pollut. Res., 26 (2019) 3262-3291.

[8] O.A. Hammadi, “Production of Nanopowders from Physical Vapor Deposited Films on Nonmetallic Substrates by Conjunctional Freezing-Assisted Ultrasonic Extraction Method”, Proc. IMechE, Part N, J. Nanomater. Nanoeng. Nanosys., 232(4) (2018) 135-140.

[9] O.A. Hammadi, M.K. Khalaf, F.J. Kadhim, “Fabrication of UV Photodetector from Nickel Oxide Nanoparticles Deposited on Silicon Substrate by Closed-Field Unbalanced Dual Magnetron Sputtering Techniques”, Opt. Quantum Electron., 47(12) (2015) 3805-3813.

[10] O.A. Hammadi, M.K. Khalaf, F.J. Kadhim, “Silicon Nitride Nanostructures Prepared by Reactive Sputtering Using Closed-Field Unbalanced Dual Magnetrons”, Proc. IMechE, Part L, J. Mater.: Design and Applications, 231(5) (2017) 479-487.

[11] M.A. Hameed and Z.M. Jabbar, “Optimization of Preparation Conditions to Control Structural Characteristics of Silicon Dioxide Nanostructures Prepared by Magnetron Plasma Sputtering”, Silicon, 10(4) (2018) 1411-1418.

[12] F.J. Al-Maliki, O.A. Hammadi and E.A. Al-Oubidy, “Optimization of Rutile/Anatase Ratio in Titanium Dioxide Nanostructures prepared by DC Magnetron Sputtering Technique”, Iraqi J. Sci., 60 (2019) 91-98.

[13] O.A. Hammadi, F.J. Al-Maliki and E.A. Al-Oubidy, “Photocatalytic Activity of Nitrogen-Doped Titanium Dioxide Nanostructures Synthesized by DC Reactive Magnetron Sputtering Technique”, Nonlinear Opt. Quantum Opt., 51(1-2) (2019) 67-78.

[14] O.A. Hammadi t al., “Operation Characteristics of a Closed-Field Unbalanced Dual-Magnetrons Plasma Sputtering System”, Bulg. J. Phys., 41(1) (2014) 24-33.

[15] O.A. Hammadi, M.K. Khalaf, F.J. Kadhim, “Fabrication and Characterization of UV Photodetectors Based on Silicon Nitride Nanostructures Prepared by Magnetron Sputtering”, Proc. IMechE, Part N, J. Nanoeng. Nanosys., 230(1) (2016) 32-36.

[16] O.A. Hammadi and N.E. Naji, “Characterization of Polycrystalline Nickel Cobaltite Nanostructures Prepared by DC Plasma Magnetron Co-Sputtering for Gas Sensing Applications”, Photon. Sens., 8(1) (2018) 43-47.

[17] O.A. Hammadi, “Characteristics of Heat-Annealed Silicon Homojunction Infrared Photodetector Fabricated by Plasma-Assisted Technique”, Photon. Sens., 6(4) (2016) 345-350.

[18] O.A. Hamadi and K.Z. Yahiya, “Optical and electrical properties of selenium-antimony heterojunction formed on silicon substrate”, J. Pure Appl. Sci., 4(2) (2007) 1-11.

 ISSN (print) 2958-8960 (online) 3006-6042 Printed in IRAQ