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Nanostructured Silicon Nitride Thin Films Prepared by DC Reactive Sputtering

Mohammed A. HAMEED, Baraa K. NASSER

Department of Physics, College of Science, University of Baghdad, Baghdad, IRAQ

Abstract

In this work, silicon nitride nanostructures were synthesized by dc reactive magnetron sputtering technique. The effect of deposition time on the structural characteristics, especially structural purity and nanoparticle size, was determined. Long deposition time allows more silicon atoms sputtered from the target to bond to nitrogen atoms and form silicon nitride molecules. Therefore, the structure of the final product is highly dominated by silicon nitride as confirmed by the x-ray diffraction pattern. On the other hand, nanoparticles with larger size were grown at long deposition time. As the deposition time was increased from 3 to 4 hours, the nanoparticle size was increased from 26.10 to 101.20 nm. The structural characteristics of silicon nitride nanoparticles can be sufficiently controlled by the preparation conditions to serve certain applications based on nanoparticle size.

Keywords: Silicon nitride; Nanoparticles; Magnetron sputtering; Reactive sputtering

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1. Introduction

Recent achievements in nanomaterials and nanotechnology have induced new practical fields to use nanostructures and nanoparticles to enhance and improve the performance of some classical scientific, engineering and technical systems. Furthermore, some new breakthroughs were found and based on the properties and characteristics of such nanostructures and nanoparticles.

Silicon nitride is a polymorphic material, presenting three crystallographic modifications designated as the α, β and γ phases [1]. The α and β phases can be produced under normal nitrogen pressure and have great importance in the production of advanced ceramics, while the recently discovered γ-phase can be formed only at extremely high pressures and has no practical use yet [2,3]. A prime driver for the development of silicon nitride was to replace metals with ceramics in advanced turbine and reciprocating engines for higher operating temperatures and efficiencies [2].

Silicon nitride has the strongest covalent bond properties next to silicon carbide. Its optical and electrical properties at nanoscale are encouraging to fabricate photonic devices by depositing nano films of silicon nitride on semiconducting substrates [4-7]. At room temperature, it has high resistivity ($\sim 10^{13}$ Ω.cm), dielectric constant of 7.0 and wide energy gap of 5.06-5.25 eV [8].

Silicon nitride thin films are common insulators in the semiconductor industry for the passivation of electronic devices because they form excellent protective barriers against the diffusion of water, sodium and potassium ions found in biological environments [9,10]. The Young's modulus of silicon nitride thin film is higher than that of silicon and its intrinsic stress can be controlled by the specifics of the deposition process. Silicon nitride is effective masking material in many alkaline etch solutions [11].

Silicon nitride is widely used as hard optical material but also has excellent piezoelectric response [12]. In addition to their numerous optical applications, silicon nitride thin films have applications in surface passivation for microcrystalline silicon solar cells, high frequency piezoelectric transducers, and biomedical applications and in nanocomposites [13-18].

In this work, the effect of deposition time on the structural characteristics of silicon nitride nanoparticles synthesized by dc reactive magnetron sputtering technique is determined. These characteristics are optimized to use the synthesized nanoparticles as scatterers in random gain media.

2. Experimental Part

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A homemade dc reactive magnetron sputtering system schematically was used in this work to synthesize silicon nitride thin films on glass substrates. The deposition chamber was initially evacuated down to 0.001 mbar then a mixture of argon and nitrogen gases (50:50) was pumped into the chamber. The maximum gas pressure was 0.07 mbar. The flow rate of the $Ar:N_2$ mixture was ranging between 20-25 cm^3/s. More details on this system can be found elsewhere [5,19-25].

The inter-electrode distance between cathode and anode was adjusted at 4 cm, the discharge voltage was maintained at 3.5 kV and the discharge current was maintained at 35-40 mA. An n-type silicon wafer with (111) orientation was used as sputtering target and mounted on the cathode by Teflon ring while the glass substrates were placed on the anode. The two electrodes could be cooled by circulating water from chiller into cooling channels inside both electrodes. The cathode was cooled to prevent the secondary electron emission, which consumes an amount of discharge power, while the anode was not cooled to support the adhesion of silicon nitride film to the glass substrate.

The silicon nitride nanopowder sample shown in Fig. (1) was extracted from thin film samples by a novel technique to extract nanopowders from thin films deposited by physical vapor deposition methods on non-metallic substrates known as conjunctional freezing-assisted ultrasonic extraction method [26]. The structural characteristics of these nanopowders were determined by x-ray diffraction (XRD) patterns, Fourier-transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

Fig. (1) The silicon nitride nanopowder extracted from thin film samples prepared in this work

3. Results and Discussion

Figure (2) shows the XRD patterns of three samples prepared after different deposition times (3, 3.5 and 4 hours). In general, the patterns are mostly amorphous, which an initial indication to the formation of nanostructures. However, few peaks can be observed and recognized to match the JCPDS card of silicon nitride [27]. The sample prepared after deposition time of 3 hours shows apparent peak at $2\theta = 32.58°$, which belongs to silicon crystallites in the structure as they did not bond to nitrogen. The samples prepared after longer times (3.5 and 4 hours) shows the same with lower intensity as the silicon atoms sputtered from the target find longer time to bond to nitrogen and hence form silicon nitride molecules. All samples show three distinctive peaks belonging to silicon nitride at 2θ of 22.84°, 46.80° and 58.18°, which correspond to the crystal planes of (110), (220) and (221), respectively. Deposition time can be considered an effective parameter to ensure the nitridization of the sputtered silicon atoms as much as possible, which takes the prepared structures to the high purity situation.

The values of crystallite size estimated by Scherrer's formula for all samples were reasonably identical (10-15 nm), which reflects the advantage of magnetron sputtering technique to prepare such ceramic compound at room temperature or little higher (27-350°C).

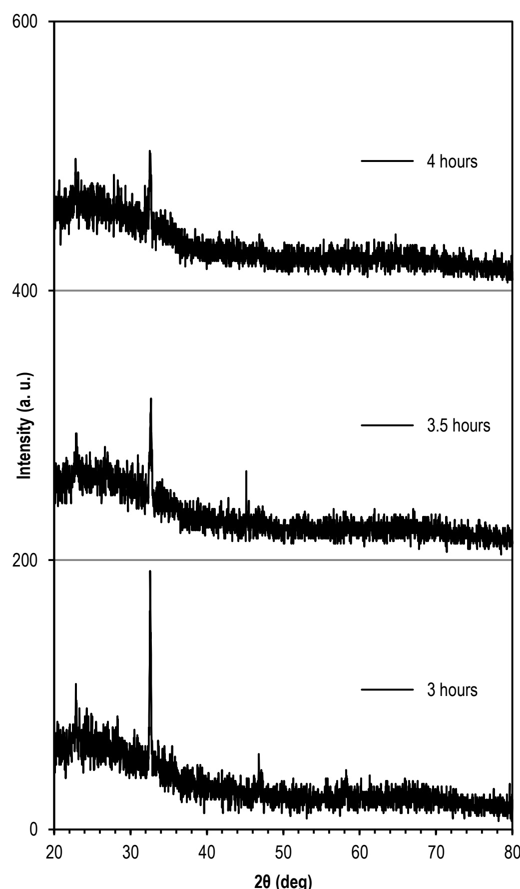

Fig. (2) The XRD patterns of silicon nitride samples prepared after different deposition times (3, 3.5 and 4 hours)

Figure (3) shows the FTIR spectrum of the silicon nitride sample prepared after deposition time of 3 hours. Two peaks of significant absorption can be seen at 900-1100 cm^{-1} on the FTIR spectrum of Si_3N_4 nanostructures prepared in this work shown in figure below. This broad band is assigned to the Si-N-Si vibration mode in Si_3N_4 molecule [28] and indicates that the formed Si_3N_4 structures are nanocrystals. The peak observed at 460-490 cm-1 is attributed to the Si-N wagging [29]. Other absorption peaks seen on the FTIR spectrum (1400-3600 cm^{-1}) may be attributed to the presence of

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some contaminations reached the silicon nitride samples when exposed to air before been tested. All prepared samples exhibited the same behavior approximately regardless the deposition time.

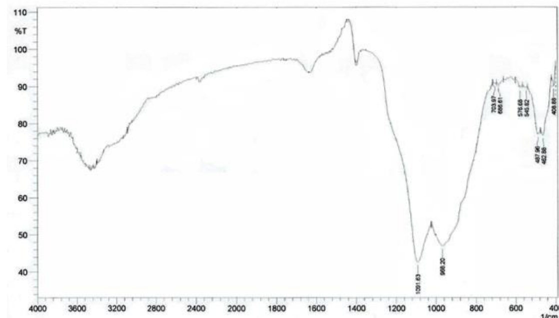
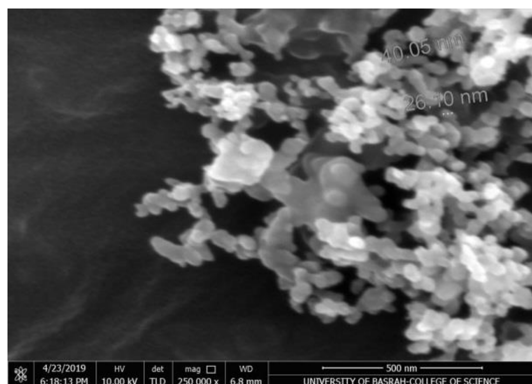


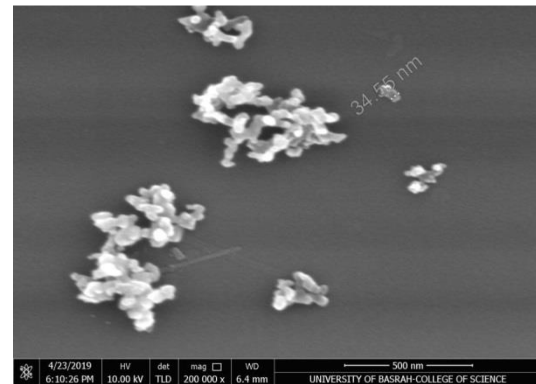
Fig. (3) The FTIR spectrum of silicon nitride sample prepared after deposition time of 3 hours

Figure (4) shows the SEM images of the three samples prepared after different deposition times (3, 3.5 and 4 hours). The formation of nanoparticles is confirmed in all samples as the particle size is in the nanoscale. The minimum particle size was determined to be 26.10, 34.55 and 101.20 nm for the samples prepared after deposition time of 3, 3.5 and 4 hours, respectively. It is clear that the particle size is increased with deposition time, which is attributed to the growth of the grains with time to form larger particles.

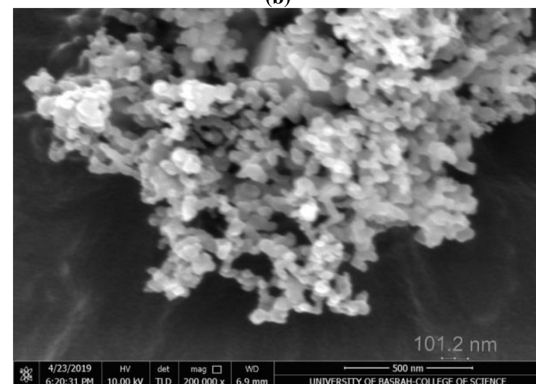
These results can be considered well to control the nanoparticle size to satisfy certain requirements of practical applications of such nanostructures. An experimental compensation is required to prepare highly pure silicon nitride nanostructures with particle size as small as possible by controlling the operation parameters and preparation conditions, especially the deposition time.



(a)



(b)



(c)

Fig. (4) The SEM images of silicon nitride samples prepared after different deposition times (3, 3.5 and 4 hours)

4. Conclusion

In concluding remarks, silicon nitride nanostructures were successfully prepared by dc reactive magnetron sputtering technique. These nanostructures exhibited high structural purity as no other compounds were found in the final samples. On the other hand, long deposition time caused to grow nanoparticles with larger size when compared to those prepared after shorter deposition time. These results are very necessary to synthesize such nanoparticles for some applications requiring highly-pure nanoparticles to be used as scatterers such as random gain media.

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