Firas J. Kadhim[1]
Ahmed A. Anber[2]

[1] Department of Physics, College of Science, University of Baghdad, Baghdad, IRAQ
[2] Department of Physics, College of Science, University of Wasit, Wasit, IRAQ

Microhardness of Nanostructured Si_xN_{1-x} Thin Films Prepared by Reactive Magnetron Sputtering

Nanostructured silicon nitride (Si_xN_{1-x}) thin films were prepared by reactive magnetron sputtering using Ar/N_2 gas mixture of 1:1. The structures and fractional compositions of the prepared samples were determined by x-ray diffraction (XRD) and electron-dispersion x-ray diffraction (EDS) patterns as functions of inter-electrode distance. They showed that the prepared films were polycrystalline and the partial amount of silicon (x) is ranging in 0.825-0.865 as the inter-electrode distance was ranging in 2.5-7.5cm. The particle sizes of the prepared nanostructured were determined by the field-effect scanning electron microscopy (FE-SEM) to be about 38nm. Also, the highest value of the surface roughness of the prepared nanostructures was determined by the atomic force microscopy (AFM) and found to increase with increasing inter-electrode distance to be 29.00nm for the samples prepared at 7.5cm. The measured Vickers microhardness of the prepared films showed relatively high values (570-750) and was decreased with decreasing film thickness, which is inversely proportional to the inter-electrode distance. However, no uniform relation between the microhardness and fractional composition of the prepared sample was observed.

Keywords: Silicon nitride; magnetron sputtering; Nanostructures; Microhardness
Received: 2 May 2016; **Revised**; 7 June 2016; **Accepted**: 19 June 2016

1. Introduction

Reactive magnetron sputtering technique can be used to produce smooth and well-adherent coatings. Its ability to scale up the process makes it a good technique in manufacturing of machine elements [1]. Polycrystalline structures can be deposited to form a preferred orientation under certain sputtering conditions such as high substrate bias [2]. Enhancements in the microhardness of such polycrystalline structures depend on this microstructural characteristic. Proper control of the preferred orientation through deposition could therefore lead to greater hardness enhancements [3,4].

It is well known the improvement on the strength of materials by grain refinement. The Hall–Petch equation relates the yield stress, and thus the hardness, with the inverse of the square root of the grain size. However, many authors reported an inverse of this law when the grain size decreases down to values lower than 10-20 nm [5]. The use of mechanically resistant coatings is a common practice in many industries [6]. Thin films and coatings are of increasing interest for use in compact electronic components [7-9], micromechanical systems [10-12], and for decorative purposes [10]. In order to develop additional surface functions, such as excellent abrasion and corrosion resistance in materials, hard films deposited by physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques have been widely applied in recent years [14-16].

Silicon nitride was developed in the 1960s and 1970s in a search for fully dense, high strength and high toughness materials. A prime driver for its development was to replace metals with ceramics in advanced turbine and reciprocating engines for higher operating temperatures and efficiencies [17]. Silicon nitride films are commonly prepared by CVD techniques. These films contain relatively high amounts of hydrogen, which can lead to a degradation of films in subsequent high-temperature processing steps [18]. Therefore, sputtering is an interesting thin film deposition technique for all silicon nitride applications where low processing temperatures are desired, low hydrogen contents in the films are required because no hydrogen content is obtained, or the stoichiometry of the films should be controlled – for example – to obtain high hardness of the film [19,20]. Hardness values have been estimated for silicon nitride by molecular dynamics calculations, giving values of 31.5-50.3 GPa [21,22]. To evaluate the quality of such thin films, it has become increasingly necessary to measure their mechanical properties, mainly the microhardness. The actual composition of the films can be varied within certain range by adjusting the deposition conditions, including reactant gas mixing ratio and pressure, substrate temperature and plasma power [23,24].

Silicon nitride has the strongest covalent bond properties next to silicon carbide. 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 [25].

In this work, nanostructured silicon nitride (Si_xN_{1-x}) thin films are prepared by reactive magnetron sputtering and their structures and fractional compositions are studied as functions of inter-electrode distance. Also, the Vickers microhardness of the prepared films is studied and related to the fractional composition and surface roughness of the final product in order to introduce the possibility to use them in tribology applications.

2. Experiment

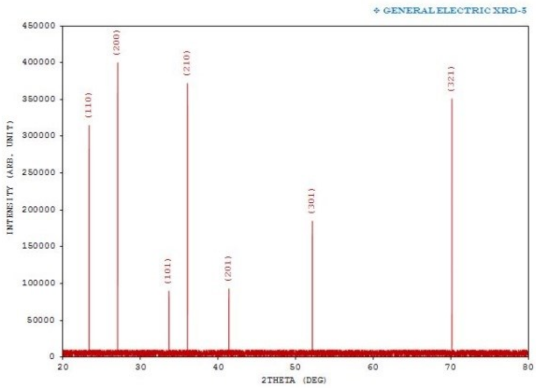
Silicon nitride thin films were deposited on glass substrates by sputtering of a p-type silicon target using a reactive dc magnetron sputtering system. Highly-pure argon (Ar) and nitrogen (N_2) gases were used as sputtering and reactive gases, respectively. The mixing ratio of Ar:N_2 was 1:1 as they were mixed in an external mixer before allowed to enter the discharge chamber, which was initially evacuated down to 10^{-3} mbar.

The operation conditions include working gas pressure of 0.02 mbar, discharge voltage of 3.5 kV and discharge current of 40-45 mA. The inter-electrode distance could be varied from 2.5 to 7.5 cm. The cathode electrode, on which the silicon target was maintained, was cooled down to 3°C, while the anode temperature (which is approximately equal to substrate temperature) was kept at 250°C. The deposition time was 150 min.

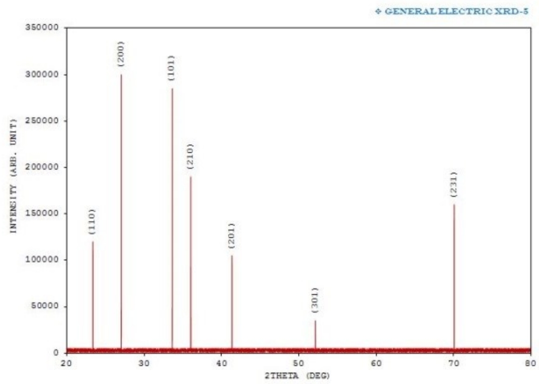
A Bruker X-Ray Diffractometer instrument with 1.54.5Å CuKα radiation was used for the x-ray diffraction measurements. The field-effect scanning electron microscopy (FE-SEM) and electron dispersion x-ray diffraction (EDS) were carried out using TESCAN Vega EasyProbe instrument. The Vickers microhardness was measured by a Laryee HVS-1000 instrument. An empty substrate was used as a reference for microhardness measurements before performing the measurement on film deposited on such substrate. The Vickers microhardness of empty substrate was 532.9.

3. Results and Discussion

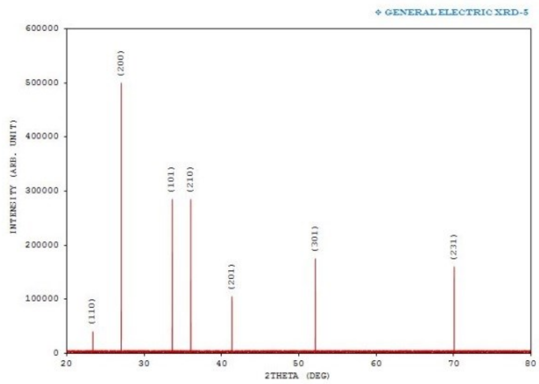
Figure (1) shows the XRD patterns of the silicon nitride thin films deposited on glass substrates and prepared at different inter-electrode distance. It is clear that these films are polycrystalline and include seven main crystal planes of (110), (200), (101), (210), (201), (301) and (321). Also, in all samples, the crystal plane of (200) exhibits the highest intensity amongst all grown planes. Therefore, further control of the inter-electrode distance can be performed to obtain as less as possible number of crystal planes (or single-crystalline film) with featured properties for certain applications of silicon nitride thin films.



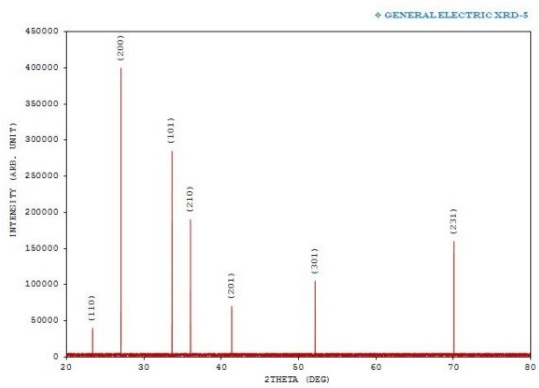
(a)



(b)



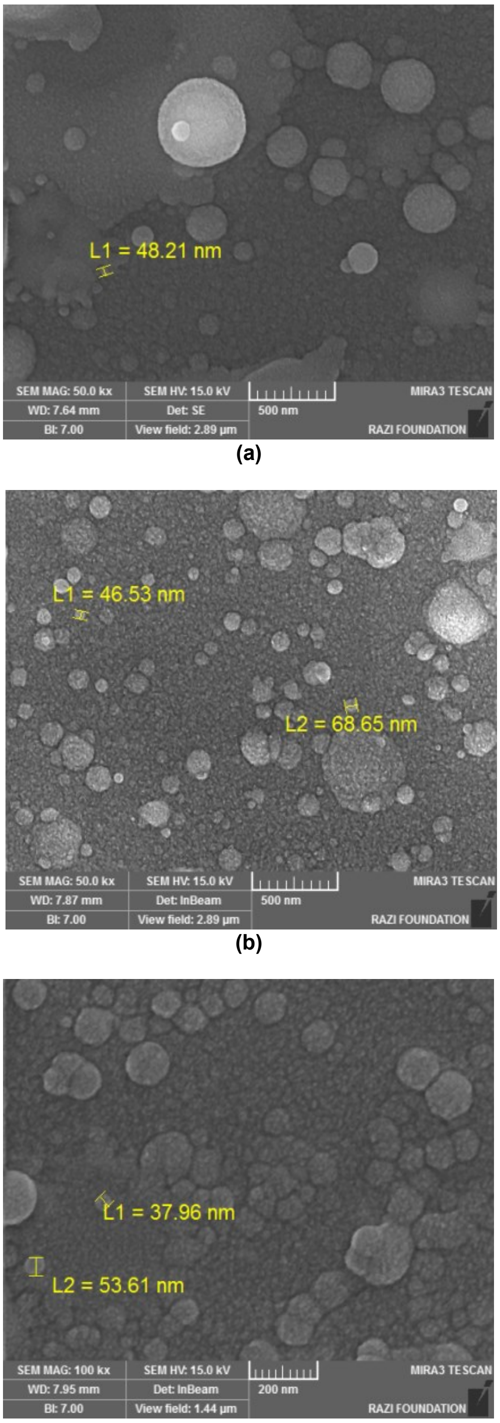
(c)



(d)

Fig. (1) XRD patterns of the silicon nitride samples prepared at different inter-electrode distances (a) 2.5 (b) 3.5 (c) 4.5 and (d) 7.5 cm (Ar:N_2 gas mixture is 1:1)

One of the most important features of the polycrystalline structures of ceramics, such as silicon nitride, is the high hardness. This feature is partially attributed to the interference of different crystal planes as they support each other against mechanical forces applied to the surface of ceramic sample.



(a)

(b)

(c)

Fig. (4) FE-SEM of the silicon nitride nanostructures prepared at 1:1 mixing ratio of Ar:N_2 and inter-electrode distance of (a) 2.5, (b) 4.5 and (c) 7.5 cm

Figure (2) shows the FE-SEM image of the silicon nitride nanostructures prepared at 1:1 mixing ratio of Ar:N_2 and different inter-electrode distances (2.5, 4.5 and 7.5). As shown, approximately uniform shaped particles (spherical) were grown. It was experimentally confirmed that the thickness – as well as particle size – of silicon nitride film grown by magnetron sputtering is decreasing with increasing the inter-electrode distance [26]. In this work, the minimum particle size of 48.21, 46.53 and 37.96nm can be observed for samples prepared at 2.5, 4.5 and 7.5cm, respectively.

The formation of large particle size – and then clusters – in samples prepared at smaller distances is attributed to the higher rate of deposition as the continuously formed nanoparticles might locate on other nanoparticles those already positioned on the substrate; therefore, they did not find empty positions and forced to cluster with other nanoparticles. At larger distances, nanoparticles might have good opportunity to locate on the substrate as those coming later might find empty locations to deposit on instead of accumulate over deposited ones.

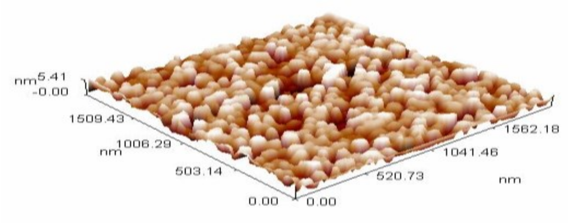
Combining the XRD and SEM results, the growth of minimum number of crystal planes as well as minimum nanoparticle size can be governed by controlling the operation parameters, especially the inter-electrode distance and gas mixing ratio.

Figure (3) shows the 3D AFM images of the silicon nitride nanostructures prepared at 1:1 mixing ratio of Ar:N_2 and different inter-electrode distances (2.5, 4.5 and 7.5cm). As shown in table (1), it is observed that the average surface roughness of these nanostructures was increased from 5.41nm for the sample prepared at 2.5cm to 29.00nm for that prepared at 7.5cm, which may be attributed to the corresponding decrease in particle size, as confirmed before by the FE-SEM results. Recently, it has become clear that characterizing the surface roughness provides much better understanding of material's microstructure and hence many of their effective properties.

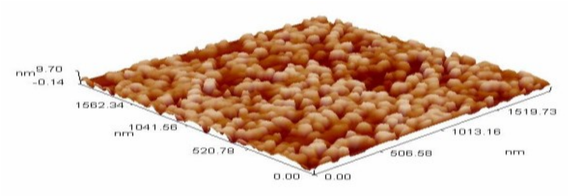
Table (1) Minimum particle size (D) and average surface roughness (R_a) of the prepared nanostructures as a function of the inter-electrode distance (d)

d (cm)	D (nm)	R_a (nm)
2.5	48.21	5.41
4.5	46.53	9.70
7.5	37.96	29.00

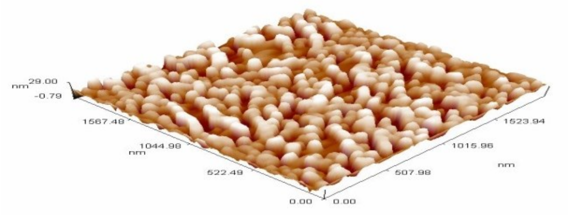
Figure (4) shows the variation of measured Vickers microhardness of the silicon nitride films with the inter-electrode distance at which these films prepared. The microhardness decreases by 18% as the inter-electrode distance was increased by 200% (from 2.5 to 7.5cm) as the film thickness was accordingly decreased. Mechanically, the hardness is a function of the film thickness. However, the nanostructured film samples may exhibit higher hardness values than the bulk samples due to the condensed surface area, which may exceeds two orders of magnitude. This feature is dependent of the fractional composition of the prepared sample and table (2) shows the relation of measured Vickers microhardness to the fractional composition of Si_xN_{1-x} samples prepared at different inter-electrode distances.



(a)



(b)



(c)

Fig. (4) 3D AFM of the silicon nitride nanostructures prepared at 1:1 mixing ratio of Ar:N_2 and inter-electrode distance of (a) 2.5, (b) 4.5 and (c) 7.5 cm

Table (2) The relation of Vickers microhardness to the composition of the prepared sample (Si_xN_{1-x})

d (cm)	Si (%)	N (%)	Si_xN_{1-x}	H.V.
2.5	71.0	15.1	$Si_{0.825}N_{0.175}$	678.9
4.5	76.7	12.0	$Si_{0.865}N_{0.135}$	630.7
7.5	71.0	13.5	$Si_{0.84}N_{0.16}$	554.2

4. Conclusions

In concluding remarks, structures and fractional compositions of nanostructured silicon nitride (Si_xN_{1-x}) thin films prepared by reactive magnetron sputtering using Ar/N_2 gas mixture of 1:1 showed that these films were polycrystalline and the partial amount of silicon (x) is ranging in 0.825-0.865 as the inter-electrode distance was ranging in 2.5-7.5cm. Combining the XRD and SEM results, the growth of minimum number of crystal planes as well as minimum nanoparticle size can be governed by controlling the operation parameters, especially the inter-electrode distance and gas mixing ratio. The surface roughness of the prepared films was increasing with the inter-electrode distance and their measured Vickers microhardness showed relatively high values and was decreased with increasing the inter-electrode distance. However, no uniform relation between the microhardness and fractional composition of the prepared sample was observed.

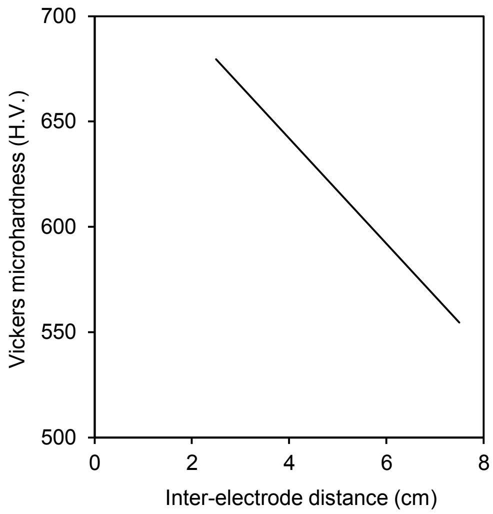


Fig. (4) Vickers microhardness of the prepared silicon nitride thin films as a function of inert-electrode distance

References

[1] F. Svahn, Å. Kassman-Rudolphi and E. Wallén, *Wear*, 254, 1092-1098 (2003).
[2] P. Yashar et al., *J. Vac. Sci. Technol. A*, 16, 2913-2918 (1998).
[3] Q. Yang et al., *Scripta Materialia*, 46, 293-297 (2002).
[4] A. A. Turkin et al., *J. Appl. Phys.*, 105, 013523-1-7 (2009).
[5] A. Cavaleiro and C. Louro, *Vacuum*, 64, 211-218 (2002).
[6] M.J. Powell, B.C. Easton and O.F. Hill, *Appl. Phys. Lett.*, 38, 794 (1981).
[7] H.E. Moes and E. Vanderkerckhave, in *Silicon Nitride and Silicon Dioxide Thin Insulating Films*, edited by V.J. Kapoor and K.T. Hankins (The Electrochemical Society, Pennington, NJ, 1987).
[8] A.K. Sinha, *Solid State Technol.*, 133, April (1980).
[9] A.R. Reinberg, *J. Electron. Mater.*, 8, 345 (1979).
[10] J.L. Vössen and W. Kern, **"Thin Film Processes"**, Academic Press (London, 1978).
[11] J. Musil, J. Vyskocil and S. Kadlek, in *Physics of Thin Films*, edited by M.H. Francombe and J. L. Vossen (Academic, San Diego, 1993), Vol. 17.
[12] H.Y. Yang, N. Niimi and G. Lucovsky, *J. Appl. Phys.*, 83, 2327 (1998).

[13] B. de Salvo *et al.*, *J. Appl. Phys.*, 86, 2751 (1999).
[14] N. Lustig and J. Kanicki, *J. Appl. Phys.*, 65, 3951 (1989).
[15] F. Chen et al., *J. Appl. Phys.*, 90, 1898 (2001).
[16] C. Savall, J.C. Bruyére and J.P. Stoquert, *Thin Solid Films*, 260, 174 (1995).
[17] J.C. da Conceição Lorenzzi, Boron nitride thin films deposited by magnetron sputtering on Si_3N_4, PhD thesis, Universidade de Aveiro, Departamento de Engenharia Cerâmica e do Vidro, pp. 10-16 (2007).
[18] M. Vila et al., *Nucl. Instrum. Meth. Phys. Res.*, B211, 199 (2003).
[19] H. P. Löbl and M. Huppertz, *Thin Solid Films*, 317, 153 (1998).
[20] P. Walsh et al., *Appl. Phys. Lett.,* 82, 118 (2003).
[21] R. Vernhes et al., *Appl. Opt.*, 43, 97 (2004).
[22] M. Vila, D. Caceres and C. Prieto, *J. Appl. Phys.*, 94(12), 7868-7873 (2003).
E.P. Donovan et al., *Appl. Opt.*, 28, 2940 (1989).
[23] P.L. Swart, P.V. Bulkin and B.M. Lacquet, *J. Non-Cryst. Solids*, 187, 484 (1995).
[24] V.P. Tolstoy, I.V. Chernyshova and V.A. Skryshevsky, **"Handbook of Infrared Spectroscopy of Ultrathin Films"**, John-Wiley & Sons, Inc. (NJ), 2003, p.435.
[25] S.A. Awan, R.D. Gould and S. Gravano, *Thin Solid Films*, 335-356, 1999, p. 456.
[26] O.A. Hammadi, "Design and Construction of Closed Field Unbalanced Magnetron of Plasma System to Prepare Nano Thin Film Detector", PhD thesis, University of Baghdad (Iraq) (2014).

- *First reviewer at Department of Physics, Faculty of Science, Kobe University, JAPAN*
- *Second reviewer at Department of Physics, Faculty of Science, University of Craiova, ROMANIA*

