Digest Journal of Nanomaterials and Biostructures Vol. 12, No. 1, January - March 2017, p. 111 - 117

PHOTOLUMINESCENCE IN NANOSTRUCTURED ALPHA-SILICON NITRIDE COATINGS (α-Si_3N_4)

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In this work α-Si_3N_4 coatings grown by hybrid chemical vapor deposition system (HYSY-CVD) are presented. Two different morphologies, pores and fibers, were obtained using two different flows, 45 ml/min (flow 1) and 60 ml/min (flow 2) over a period of 120 min, of nitrogen:ammonia gas mixture (95%:5%). This coatings presents nanocrystals of 20 nm and 36 nm for 1 and 2 flows, respectively, this parameters were obtained by Debye-Scherer formulation. Band gaps of 1.95eV for flow 1 and 1.90 eV for flow 2 were derived from UV-Vis reflectance. The Photoluminescence spectra reveal emissions at 477 nm for flow 1 and 470 nm for flow 2.

(Received November 16, 2016; Accepted February 1, 2017)

Keywords: Ceramic Material, Coatings, HYSY-CVD, Nanostructured Material, α-Si_3N_4.

1. Introduction

Silicon nitride is a ceramic material with a bandgap energy of about 5.3 eV, although there are reports of others energy bandgap ranging from 4.2 eV to 5.3 eV the. This material presents some interesting properties such as good resistance to high temperatures, high corrosion resistance, thermal shock resistance, high stability in viscosity and low thermal expansion [1, 2, 3].

In recent years, the emission of light in silicon based materials has brought important contributions in optoelectronics area and in display applications [4, 5].

Nanostructured silicon nitride, especially the fiber-like morphology, has received much interest because of its properties as can be used in the electronics field since it has resistance to high temperature, high frequency and is friendly with the environment [6]. A green emission was found in a silicon structure which provides the possibility of creating devices of all emission colors based on silicon-based technologies [7].

In the amorphous silicon nitride were found emissions in the green and in the alpha type were found emissions in the blue.

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2. Experimental details

The α-Si_3N_4 coatings were made in a hybrid chemical vapor deposition system (HYSY-CVD) which is named because a precursor salt of Na_2SiF_6 is used in the reactor to obtain the SiF_4 gas. Which is combined with ammonia to obtain the silicon nitride. In the reactor, a flow of ammonia nitrogen gas mixture was circulated with 95%: 5% percentages respectively at flows of 45 ml / min and 60 ml / min over a period of 120 min and were deposited on substrates of type N silicon 111. The salt was placed at 550 ° C and the substrate at 900 ° C into the reactor.

3. Characterization equipment

A scanning electron microscope JSM JEOL model 6300, a Brucker D8 X-ray diffractometer, a Horiba Jobin Yvon brand fluorometer the fluorolog -3 model and a UV-VIS model USB2000+XR1-ES spectrometer.

4. Results and discussion

In the scanning electron microscope images are observed the two types of coatings, one in the form of fibers and another porous as shown in Figs. 1 and 2.

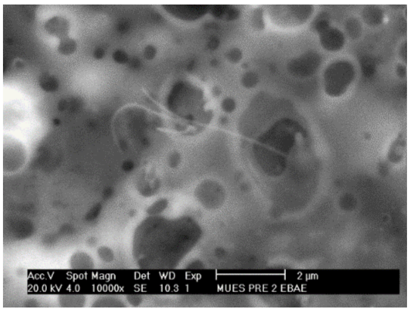

Fig. 1. Porous silicon nitride coating

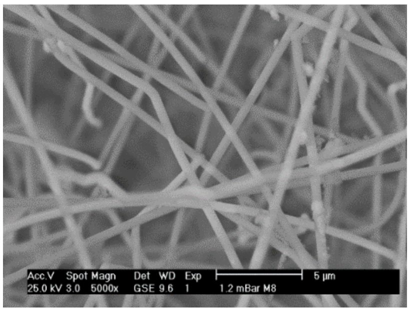

Fig. 2. Silicon nitride fiber-like coating

Calculations were made to obtain the grain sizes of our coatings by implementing the Debye Scherer approximation, using the following diffraction patterns obtained in figures 3 and 4 [8]. For the pattern of figure 1 were taken the three most intense peaks being these 101 102 and 201 and averaged the results. For figure 2 was taken the most intense peak corresponding to the silicon nitride in the diffractogram, which is 101.

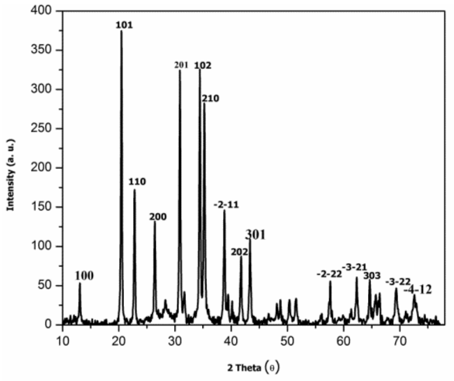

Fig. 3. Diffraction pattern of α-Si_3N_4 coating with fiber morphology.

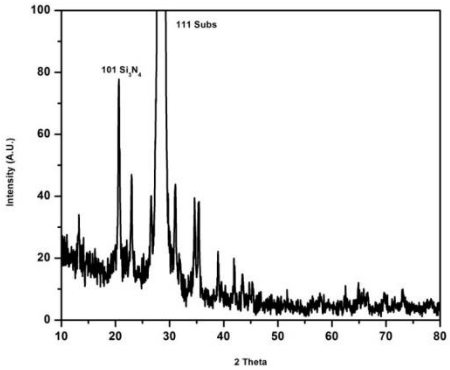

Fig. 4. α-Si_3N_4 diffraction pattern of porous coating

For a more reliable calculation, were performed peaks with Lorentz functions, as shown in Figures 5, 6, 7 and 8. Obtaining grain sizes 36 nm for the deposit in the form of fibers and 20 nm for the deposit porous.

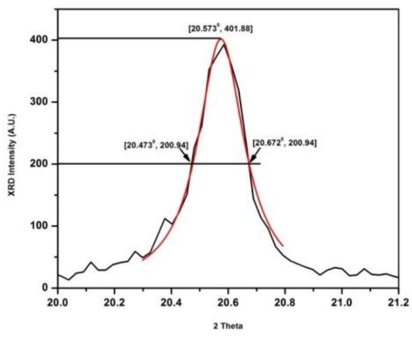

Fig. 5. 101 peak approximations with Lorentz function

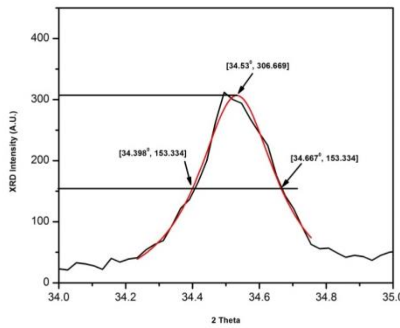

Fig. 6.102 peak approximations with Lorentz function

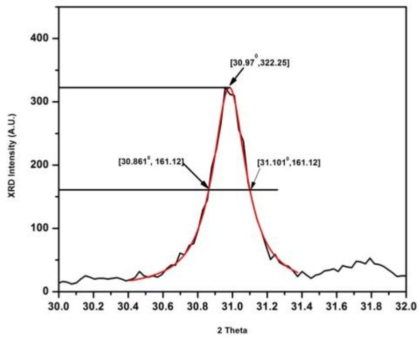

Fig. 7. 201 peak approximation with Lorentz function

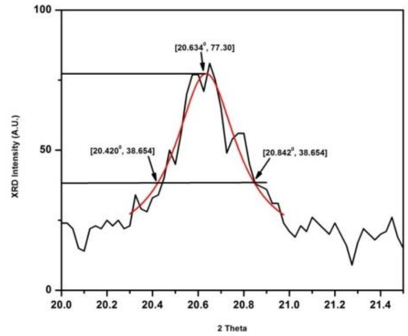

Fig. 8. 101 peak approximation with Lorentz function

Once the grain sizes were attained it was proceed to measure the optical band gap of the material using the specular reflectance technique in which the following answers were obtained: in figures 9 and 10. These were used to calculate the absorption values taking into account that there is no transmission due to the silicon substrate and normalizing the response by dividing by the maximum. Once the above was done, the optical density was plotted by the squared energy against the energy in eV to obtain the parabola and plotting a tangent line in the curvature of the parabola to obtain the optical band gap Figs 11 and 12.

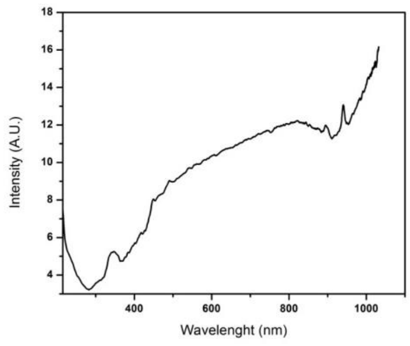

Fig. 9. Reflectance spectrum UV-Vis of fiber- like coating

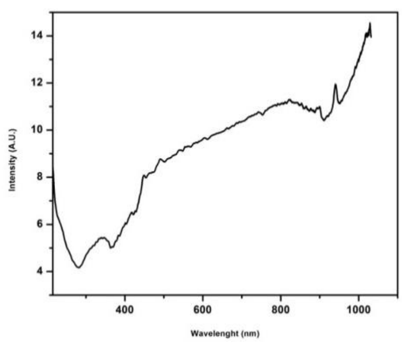

Fig. 10. Reflectance spectrum UV-Vis of the sample porous.

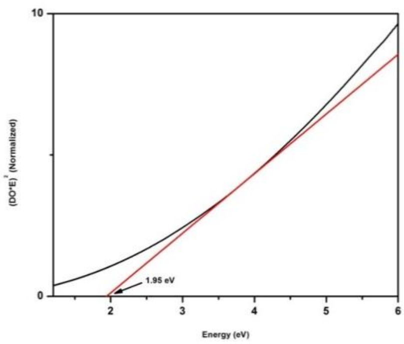

Fig. 11.Covering optical band gap, in fiber- like shades

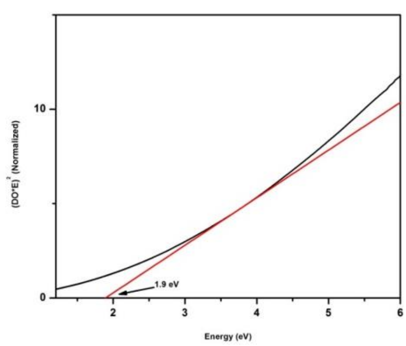

Fig. 12. Optical band gap of the porous coating

As can be seen in Figs. 11 and 12 the band gap has values of 1.95 and 1.95 eV respectively, however the reported values of silicon nitride are higher than 4.6 eV. Due to the interface of silicon and silicon nitride this value decreases significantly up to 1.9 0 2 eV [7].

Photoluminescence in alpha-type silicon nitride.

The samples were irradiated with light in the ultraviolet range at 362 nm taking into account the excitation curve of the sample were obtained the following graphs.

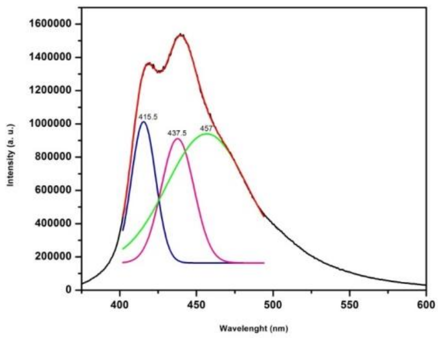

Fig. 13. Emission spectrum of the fiber coating.

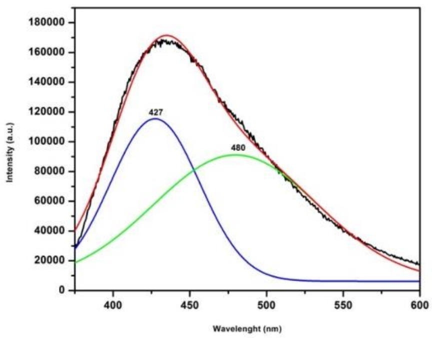

Fig. 14. Emission spectrum of the porous coating.

In the spectrum of Figures 13 and 14 can be observed emissions in the range of the blue light, due to defects in the crystalline network by entrapped ions, these defects are by ions $=N^0$ which is an energetic state Of nitrogen, $=N^-$ and a more energetic state of nitrogen, there are other contributions due to silicon ion ($\equiv Si^0$, $\equiv Si^-$ and ≡ Si-Si≡). In this case the emissions are more intense due to the silicon nitride matrix in which these defects are found, due to its grain size of 36 and 20 nm respectively, allows us to have a greater number of these defects in the crystalline network [6, 9].

To ensure that the emission is in blue chromaticity curves were made and the emissions were confirmed at the wavelengths of 470 nm for fiber coating and 477 nm for the porous coating figures 15 and 16.

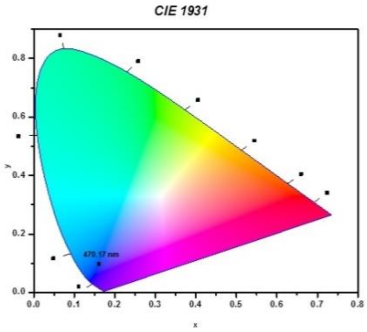

Fig. 15. Emission of fibers coating.

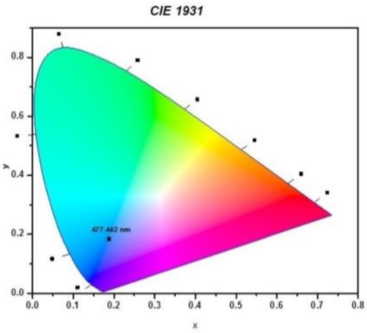

Fig. 16. Emission of porous coating.

5. Conclusions

Were attained emissions in the blue making it a good candidate for applications in that wavelength, likewise, the compounds of group III - N such as AlN and GaN. The method of obtaining allows us to have grain sizes smaller than 40 nm and because of that it is possible to have a greater number of deformations type = N^0, =N^-, ≡Si^0, ≡Si^- and ≡Si-Si≡ in the network which generates the emission in the blue. The band gap values correspond to the interface Si: Si3N4 which is around 1.9 to 2 eV.

Acknowledgement

Authors gratefully acknowledge CONACyT for financial support under contract No. SEP-CONACYT 180732.

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