

## NANOSTRUCTURED FIBERS OF $\alpha$ - $\text{Si}_3\text{N}_4$ DEPOSITED BY HYSY-CVD

E. B. ACOSTA-ENRIQUEZ<sup>a\*</sup>, M. C. ACOSTA-ENRIQUEZ<sup>b</sup>,  
R. CASTILLO-ORTEGA<sup>c</sup>, M. A. E. ZAYAS<sup>b</sup>, M. I. PECH-CANUL<sup>d</sup>

<sup>a</sup>*Departamento de Física, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, C.P. 83000, Hermosillo, Sonora, México.*

<sup>b</sup>*Departamento de Investigación en Física, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, C.P. 83000, Hermosillo, Sonora, México.*

<sup>c</sup>*Departamento de Ingeniería Industrial, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, C.P. 83000, Hermosillo, Sonora, México.*

<sup>d</sup>*Centro de Investigación y Estudios Avanzados del IPN, Unidad Saltillo, Avenida Industria Metalúrgica No. 1062, Parque Industrial Saltillo-Ramos Arizpe, 25900 Ramos Arizpe, COAH, México*

The alpha type silicon nitride nanostructured fibers were obtained by hybrid system chemical vapor deposition (HYSY-CVD) method, with low manufacturing costs, fabricating good quality deposits at atmospheric pressure. The  $\alpha$ - $\text{Si}_3\text{N}_4$  fibers on silicon wafers <111> were produced with a diameter between 400 to 500 nm using a temperature of 1200 °C. FTIR showed that the deposit is free of hydrogen and study shows Raman vibrational modes corresponding to  $\alpha$ - $\text{Si}_3\text{N}_4$ .

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### 1. Introduction

$\text{Si}_3\text{N}_4$  is a ceramic material with important properties among which are fracture and tensile strength resistance, dielectric properties, thermal shock resistant and optical radiation [1-3]. It has allowed many applications including semiconductor and aerospace industries, MEMs, thin films transistors, and solar cells [4,5]. Recent researches describe an optical respond in blue emission, by this reason the study and fabrication of this material is important [6,7].

Several fabrication methods are employed in order to grow  $\text{Si}_3\text{N}_4$  such as atmospheric chemical vapour deposition (APCVD), low pressure chemical vapour deposition (LPCVD), and plasma chemical vapour deposition (PECVD) [8,9]. However, these techniques use explosive and highly pollutant precursors. A better alternative method is hybrid system chemical vapour deposition (HYSY-CVD) that uses a solid salt as a precursor combined with mixed gas using atmospheric pressure therefore reduces costs, pollution and explosive risk [10,11].

### 2. Experimental development

In this section the three phases involved in the HYSY-CVD method are described. First, the chemical reaction that takes place in the process, then the schematic diagram of the system and finally the experiment.

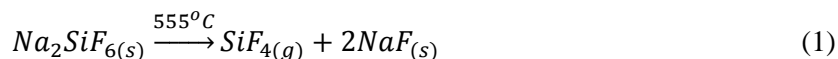
#### Chemical reaction

Sodium hexafluorosilicate salt ( $\text{Na}_2\text{SiF}_6$ ) is used as precursor which dissociates at a temperature of 555 °C into  $\text{SiF}_4$  and NaF. Using a gas mixture of nitrogen and ammonia with a

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\*Corresponding author: eulices\_acosta@hotmail.com

flow passing controlled at 900 °C the ammonia is dissociated obtaining Si<sub>3</sub>N<sub>4</sub>.



### HYSY-CVD Schematic diagram

The HYSY-CVD consists of a tubular furnace with alumina tube. The reactant gas is controlled to the system input by a flowmeter, the system output is divided in two stages, the first have an inner tube where solid waste fall around here, where there is water to neutralize the gases remaining in this area. The second is a bubbler where the water level depends on the pressure that maintains the system (see Fig. 1). The salt tablet and the substrate are placed on alumina tube.

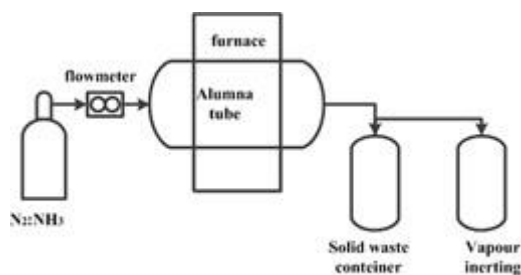


Fig. 1. Schematic diagram of HYSY-CVD.

### Experiment

The silicon nitride was obtained by HYSY-CVD method for the formation a precursor salt sodium hexafluorosilicate (Na<sub>2</sub>SiF<sub>6</sub>) which is our source of silicon, with the advantage that this salt have a low dissociation temperature.

We profit 10 grams of salt and applied a pressure of two tons. The system is formed by a Thermolyne 59300 oven, an alumina tube, a salt tablet and a N type silicon substrate.

Is important to emphasize that the tube is subjected to a temperature between 1200 and 1300 °C and a N<sub>2</sub>: NH<sub>3</sub> 95%: 5% gas mixture at a flow of 45 and 60 ml/min a time of 1.5 to 2 H is circulated through it. The salt tablet is placed at a temperature between 500 and 600°C. The substrate of N type silicon with orientation (111) is settled in the middle of the tube where the silicon nitride was deposited. The wafer temperature was varying from 1100 to 1200 °C, the system pressure was 1 ATM.

Before the experiment, the silicon wafers where washed with soap and water, then removed oil with tri-distilled water and finally cleaned with ethyl alcohol. Previously the wafers were cut into squares of 1 cm x 1 cm.

### Characterization methods

In order to obtain the structural performance of the silicon nitride, the X-ray diffraction equipment Brucker D8 was used. The morphology was observed using a scanning electron microscope JSM a JEOL model 6300. In addition, the Raman and the FTIR spectra were make with a Horiba JobinYvon HR Labram 632.8 nm (red) and a Perkin Elmer model spectrum two in a UART module, respectively for the chemical composition.

## 3. Results and discussion

The X Ray diffraction patterns, depicted in Fig. 2, show peaks of alpha silicon nitride corresponds to a hexagonal crystal structure according to the crystallographic letter [01-076-1409] database PDF-2 2004.

In Fig. 3a the SEM micrographs were described, showing the nanostructured fibers morphology with 400 at 500 nm diameters in average, the EDX analysis describes the following composition of elements Si, N, Al, O, Na with percentages 55.89%, 33.94%, 2.57%, 6.70%, 0.9%, respectively (see Fig. 3b). Aluminum and oxygen appear because of the alumina tube and the sodium is present by the salt precursor.

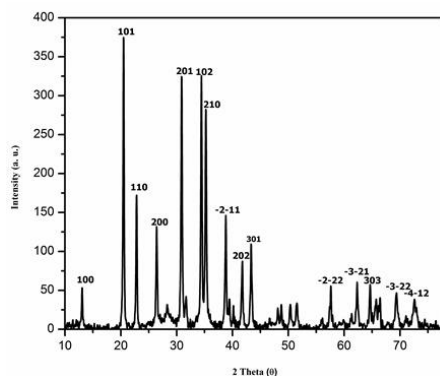


Fig. 2. The pattern XRD

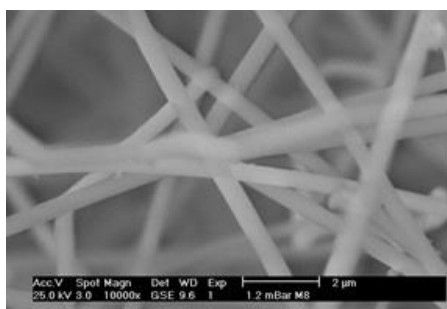


Fig. 3a. SEM image.

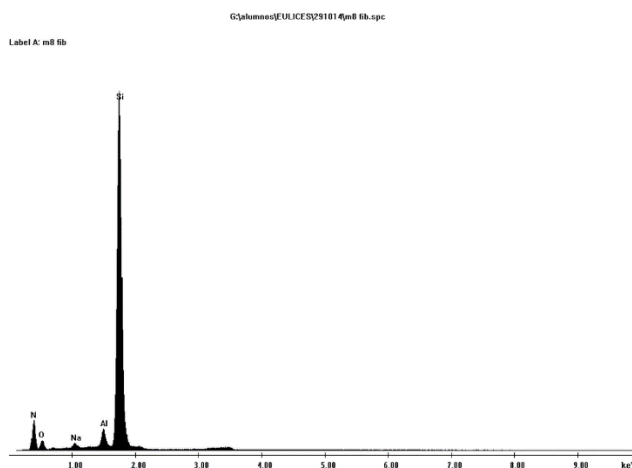


Fig. 3b. EDX image.

The Raman spectrum exhibits peaks concur those reported by Wada in 1981[12]. For the alpha type silicon nitride presents the peaks of appearing  $258$ ,  $363$  and  $459$   $\text{cm}^{-1}$  as the main vibrational mode and peaks between  $680$  and  $1000$   $\text{cm}^{-1}$  which coincide modes reported by Fu, Li and Cao in 2014[13]. The peaks located at  $258$ ,  $363$  and  $459$   $\text{cm}^{-1}$  can be interpreted as Si-N-Si symmetric vibrational modes and Raman peaks high frequency ( $680$ - $1000$   $\text{cm}^{-1}$ ) concord to

internal vibrations of silicon nitride, and the intermediate peak corresponds to vibration of the unit cell of silicon nitride the peaks were observed in the Fig.4.

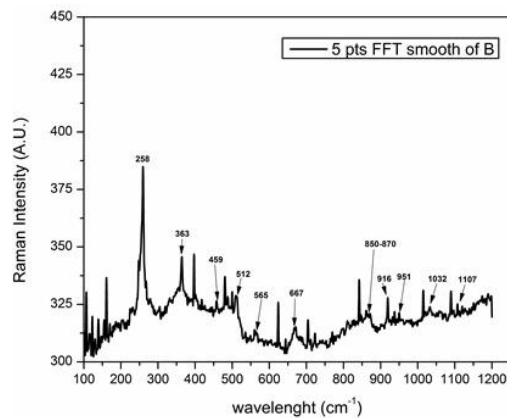


Fig. 4. Raman Spectrum of  $\alpha$ - $\text{Si}_3\text{N}_4$ .

In Figure 4, the Raman spectrum presents low intensity peaks due to the deposition of  $\text{Si}_3\text{N}_4$  ceramic powder over silicon wafer; the eleven peaks correspond to  $\alpha$ - $\text{Si}_3\text{N}_4$ .

In Fig. 5, the FTIR spectrum exhibits a peak at  $850\text{ cm}^{-1}$  resembling to Si-N, as well as the peak at  $1100\text{ cm}^{-1}$  corresponding to the presence of Si-O during the formation of silicon nitride and the substrate oxidation. It should be mentioned that the peaks appearing are Hydrogen-free which is desirable in this type of deposit. The peak of the bond N-H should be located in  $3500\text{ cm}^{-1}$  but they are not present, demonstrating that our material is Hydrogen-free.

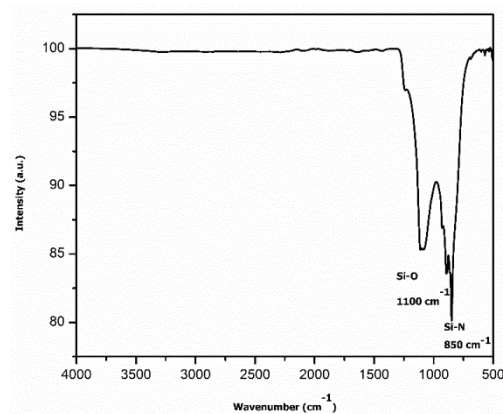


Fig. 5. FTIR of  $\alpha$ - $\text{Si}_3\text{N}_4$

#### 4. Conclusions

A deposit of alpha type silicon nitride over silicon substrates (111) was obtained. The diffraction patterns resemble to hexagonal phase silicon nitride. In the SEM micrographs can be observed the morphology of nanostructured fibers with 400 to 500 nm average diameters. The compositional analysis exhibit a greater amount of silicon and nitrogen. The Raman spectral analysis confirm the presence of silicon nitride in the coating, presenting a main peak in 258, 363, 459 and  $512\text{ cm}^{-1}$ , and secondary peaks in the range of  $600$ - $1000\text{ cm}^{-1}$ . The FTIR shows the Si-N bond at  $850\text{ cm}^{-1}$  and Si-O at  $1100\text{ cm}^{-1}$ .

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