

## Synthesis and characterization of Strontium Barium Niobate (SBN) ferroelectric thin films

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Strontium barium niobate (SBN) thin films of good quality were deposited on Si and Pt/Si substrates using a polymeric resin produced by different starting precursors. Using X-ray diffraction, the presence of SBN phase could be identified for films annealed between 500-700°C for 1 hour on both substrates. Undesired phases, such as SrNb<sub>2</sub>O<sub>6</sub> and BaNb<sub>2</sub>O<sub>6</sub>, appear crystallized in films deposited on Si over annealing temperatures between 500-700°C. However, these phases appear only at 500°C for films deposited on Pt/Si. Dielectric characterization of SBN films indicated a dielectric constant 27 and dissipation factor of 0.047 at 100 KHz. Hysteresis loops were observed at room temperature for of SBN film annealed at 700°C for 1 hour. At 100 Hz frequency, the remanent polarization, P<sub>r</sub>, and the coercive field, E<sub>c</sub>, were 18.4 mC/cm<sup>2</sup> and 147.7 kV/cm, respectively.

*Key words: SBN, thin films, ferroelectric.*

### Síntesis y caracterización de laminas delgadas ferroeléctricas de Niobato de Stroncio Bario (SBN)

Las láminas delgadas de niobato de estroncio bario de buena calidad fueron depositadas sobre sustratos de Si y Pt/Si mediante el empleo de una resina polimérica producida a partir de diferentes precursores. Por medio de difracción de rayos X se identificó la presencia de SBN para láminas tratadas entre 500-700°C durante 1 hora sobre ambos sustratos. Las fases no deseadas, como SrNb<sub>2</sub>O<sub>6</sub> y BaNb<sub>2</sub>O<sub>6</sub>, aparecen cristalizadas en láminas depositadas sobre Si tratadas entre 500-700°C. Sin embargo, estas fases aparecen solo a 500°C para láminas depositadas sobre Pt/Si. La caracterización dieléctrica de las láminas de SBN presenta una constante dieléctrica de 27 y un factor de disipación de 0.047 a 100 kHz. Las curvas de histéresis fueron observadas a temperatura ambiente para láminas tratadas a 700°C durante 1 hora. A la frecuencia de 100 Hz, la polarización remanente, P<sub>r</sub>, y el campo coercitivo, E<sub>c</sub>, fueron 18.4 mC/cm<sup>2</sup> y 147.7 kV/cm, respectivamente.

*Palabras clave: SBN, lámina delgada, ferroeléctricos.*

## 1. INTRODUCTION

Strontium barium niobate, Sr<sub>1-x</sub>Ba<sub>x</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN), has received great attention as a ferroelectric material due to its large pyroelectric coefficient, piezoelectric and electro-optic properties. The SBN is a solid solution between BaNb<sub>2</sub>O<sub>6</sub> and SrNb<sub>2</sub>O<sub>6</sub> and has a tetragonal tungsten bronze structure for x = 0.25-0.75. At room temperature the Curie temperature of SBN can be altered in the range 60-250°C, depending of the Sr/Ba ratio (1).

In recent years, SBN thin films have been prepared by several techniques such as sol-gel processing (2,3), pulsed laser deposition (4,5) and metalorganic chemical vapor deposition (MOCVD) (6,7). Large-scale processing of high-quality thin films requires low-temperature synthesis, high reproducibility and simplicity in all processing steps at low cost. Due to this fact, the search for new routes for film preparation remains as an interesting and open subject in order to improve the stability of complex solutions, the control of the stoichiometry of the film composition or to reduce the cost of the process.

In this work, SBN thin films were alternatively obtained by a chemical method. Structural, dielectric and ferroelectric properties of SBN films are presented.

## 2. EXPERIMENTAL PROCEDURE

In this work SBN films were prepared by a chemical method, used to produce a polymeric resin. The general idea is to distribute the metallic ions homogeneously throughout the polymeric resin, prepared according to the Pechini method (8,9). The process calls for forming a chelate between dissolved ions with a hydroxycarboxylic acid (citric acid). Heating of the resin in air causes a breakdown of the polymer. Subsequently, the desired crystalline phase was formed.

Barium oxide (BaO), strontium carbonate (SrCO<sub>3</sub>) and ammoniacal complex (Nb<sub>2</sub>O<sub>5</sub>-NH<sub>3</sub>-Complex) were selected as starting materials. The molar ratio of starting materials was calculated to obtain a final Sr<sub>0.75</sub>Ba<sub>0.25</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN 75/25) phase. For preparation of the resin, BaO, SrCO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub>-NH<sub>3</sub>-Complex were initially dissolved in HCl, HCl and water, respectively, to form a transparent solution. Next, each solution was mixed separately with citric acid and heated to 40°C for 30 minutes. This stage is important to form chelate between cations with a hydroxycarboxylic acid (citric acid). Then, each solution was mixed with ethylene glycol (citric acid/ethylene glycol = 50/50 in weight) and polymerized by heating up to 100°C for 30 minutes. Finally, the three solutions were mixed at room temperature and heated again to 50°C and stirred during 20 minutes to homogenization, when a transpa-

rent resin was obtained. The final transparent resin indicates that all metallic ions were distributed throughout the polymeric resin. The viscosity of the final resin was controlled with ethylic alcohol.

Resins were deposited at room temperature on Si and Pt/Si substrates by dip coating. Films were obtained by depositing multiple layers of this resin. Each layer was annealed at 400°C for one hour, to remove residual solvents, and followed by annealing between 500-700°C one hour. The process was repeated for five deposited layers to obtain a film with 0.5  $\mu\text{m}$  thickness in average. Deposited films were crack-free, uniform and well adhered on the both substrates.

The crystal structure of the films at different firing temperatures was analyzed by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation. For the electrical measurements, gold electrodes of 0.3 mm in diameter were sputter deposited on the top surface of the films deposited on Pt/Si, forming a metal-ferroelectric-metal configuration. Capacitance and dissipation factor, at 1 kHz to 10 MHz frequency were measured with a HP 4194A impedance analyzer. Hysteresis characteristics were measured by using a modified Sawyer-Tower circuit attached to a Tektronix 2232 digital oscilloscope.

### 3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of SBN films on silicon substrates, annealed at 500°C, 600°C and 700°C for 1 hour. Peaks identified in this figure were attributed mainly to tetragonal SBN phase. Some structural fluctuation can be seen in Figure 1 for films annealed at 500°C, when compared with the well-defined (001), (002) and (322) peaks of films annealed at higher temperatures. As the annealing temperature was increased, from 500°C to 700°C, these peaks in XRD patterns became sharper and the full width at half maximum decreased, indicating better crystallinity. With basis on this figure, we can see that changes of the (001) peak intensity and its full width at half-maximum (FWHM) film represents the degree of crystallization with annealing temperature.

When annealing temperature increases the intensity of the (001) peak increases and the FWHM decreases. FWHM at 500°C, 600°C and 700°C are 0.66°, 0.45° and 0.36°, respectively, meaning that increasing annealing temperature correlates with the quality of crystallization of SBN films on silicon. In addition, in Figure 1 we can identify traces of the  $\text{SrNb}_2\text{O}_6$  (SN) and  $\text{BaNb}_2\text{O}_6$  (BN) phases for films annealed between 500°C and 700°C.

Figure 2 shows XRD patterns of SBN films on Pt/Si substrate for different temperatures. As we can see, the crystallization process of SBN films on Pt/Si substrate is different as compared to films deposited on Si. The undesired SN and BN phases are present only for films annealed at 500°C for 1 hour. When annealing temperature increases these phases disappear and only a SBN phase appear at 600°C and 700°C. Thus, films deposited on Pt/Si presents better crystallinity if compared with films deposited on Si because undesired phases, such as SN and BN, do not appear for higher annealing temperatures.

For dielectric and ferroelectric measurements a film with 0.5 mm thickness, annealed at 700°C for 1 hour was used. The dielectric behavior of the SBN films, examined in terms of the dielectric constant and dissipation factor as functions of measuring frequency, are summarized in Figure 3. It may be seen that dielectric constant exhibits a slight frequency dependency, which is consistent with the expected normal behavior. The dielectric constant and dissipation factor at a frequency of 100 kHz were 27 and 0.047, respectively. The value of the dielectric constant obtained here is consistent with other reports for SBN thin films obtained through metal alkoxide (10). The frequency dependence of the dielectric constant and dissipation factor is probably related to the presence of an interfacial surface, at the interface electrodes/film, which results in an undesirable Maxwell-Wagner type dispersion in the dielectric data. Similar dielectric constant versus frequency behavior was also observed in  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  films obtained by laser ablation (11). In addition, the dielectric constant value on different top counter-electrodes varied less than 3%, indicating a good degree of uniformity in the thickness of the films.

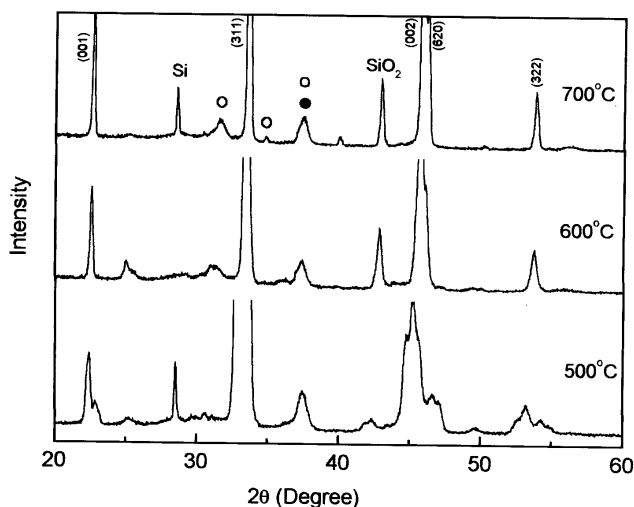


Figure 1. XRD patterns for SBN thin films deposited on silicon substrate after annealing at different temperatures. O:  $\text{SrNb}_2\text{O}_6$  (SN) ●:  $\text{BaNb}_2\text{O}_6$  (BN).

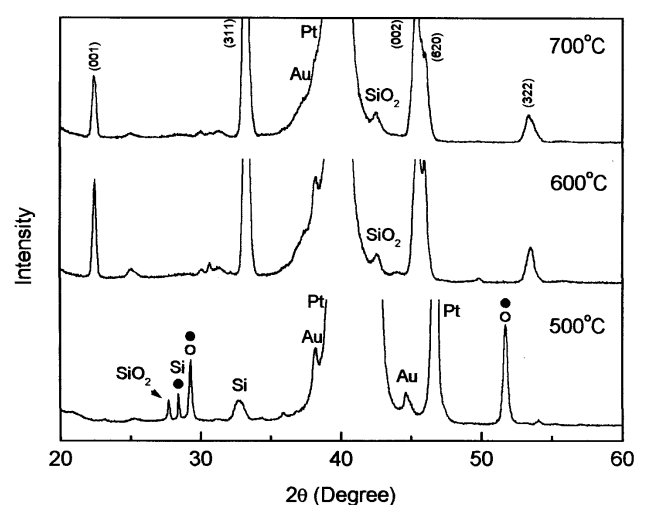


Figure 2. XRD patterns for SBN thin films deposited on Pt/Si substrate after annealing at different temperatures. O:  $\text{SrNb}_2\text{O}_6$  (SN) ●:  $\text{BaNb}_2\text{O}_6$  (BN).

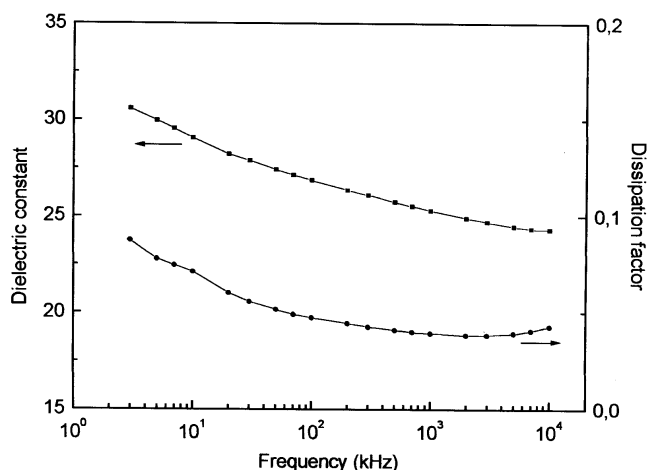


Figure 3. Dielectric constant and dissipation factor as a function of the measuring frequency for SBN films annealed at 700°C for 1 hour. Film with 0.5 $\mu$ m in thickness.

Hysteresis loops were observed at room temperature, at 100 Hz frequency. Figure 4 shows a typical P-E hysteresis loop of SBN film annealed at 700°C for 1 hour. The remanent polarization,  $P_r$ , and the coercive field,  $E_c$ , are 18.4 mC/cm<sup>2</sup> and 147.7 kV/cm, respectively. For SBN 75/25 films obtained by sol-gel values of  $P_r$  and  $E_c$  ranged from 1.9-34 mC/cm<sup>2</sup> and 51-180 kV/cm, were reported (12,10). In this work, the observed  $P_r$  is slightly lower if compared with values observed for crystals, whose values ranged from 27 to 32  $\mu$ C/cm<sup>2</sup> (13), but agree with results observed for SBN 75/25 thin films produced by others methods. However, the coercive field,  $E_c$ , and remanent polarization,  $P_r$ , values obtained here for SBN thin films may be not correspond to absolute values because conductivity effect was not discounted in loop hysteresis of the Figure 4. Thus, the distortion observed on hysteresis of the Figure 4 is probably associated with effect of conductivity in SBN film.

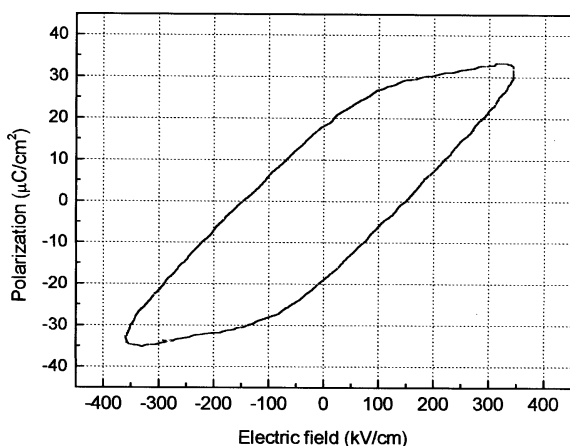


Figure 4. Hysteresis loop of SBN film annealed at 700°C for 1 hour, measured at 100 Hz frequency and room temperature.

#### 4. CONCLUSION

In conclusion, SBN thin films of good quality could be deposited on silicon using a polymeric resin produced by different starting precursors. Results showed that crystallization is better when annealing temperatures is increased up to 700°C for 1 hour. Undesired phases such as SrNb<sub>2</sub>O<sub>6</sub> and BaNb<sub>2</sub>O<sub>6</sub> appear crystallized in films deposited on Si over all annealing temperatures. However, SN and BN appear only at 500°C for films deposited on Pt/Si. Dielectric constant was measured and the ferroelectricity was confirmed by hysteresis P-E.

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