Available online at www.sciencedirect.com
SCIENCE DIRECT
Materials Chemistry and Physics 98 (2006) 203–206
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Synthesis and electrical characterization of $CaBi_2Nb_2O_9$ thin films deposited on Pt/Ti/SiO_2/Si substrates by polymeric precursor method

A.Z. Simões [a], M.A. Ramírez [a,c,*], C.S. Riccardi [a], A.H.M. Gonzalez [a], E. Longo [b], J.A. Varela [a]

[a] Chemistry Institute, UNESP—Paulista State University, C.P. 355, 14801-970 Araraquara, SP, Brazil
[b] Chemistry Department, UFSCar—Federal University of São Carlos, C.P. 676, 13560-905 São Carlos, SP, Brazil
[c] Materials Science and Technology, UNESP—Paulista State University, C.P. 473, 17033-36, Bauru, SP, Brazil

Received 25 May 2005; accepted 5 September 2005

Abstract

We report the successful deposition of $CaBi_2Nb_2O_9$ (CBN) thin films on platinum coated silicon substrates by polymeric precursor method. The CBN thin films exhibited good structural, dielectric and CBN/Pt interface characteristics. The leakage current of the capacitor structure was around 0.15 A cm^{-2} at an applied electric field of 30 kV cm^{-1}. The capacitance–voltage measurements indicated good ferroelectric polarization switching characteristics. The typical measured small signal dielectric constant and the dissipation factor at a frequency of 100 kHz were 90 and 0.053, respectively. The remanent polarization and the drive voltage values were 4.2 C cm^{-2} and 1.7 V at an applied voltage of 10 V. No significant fatigue was observed at least up to 10^8 switching cycles.

Keywords: Thin films; Annealing; Electrical properties

1. Introduction

Ferroelectric thin films have been widely investigated for their use in a variety of devices exploiting their unique piezoelectric, pyroelectric, polarization switching and electro-optic properties [1]. Recently, there has been a surge in research activity on ferroelectric thin films for nonvolatile random access memory (NVRAM) applications. Ferroelectric thin films with large remanent polarization, low coercive field and low fatigue rate characteristics have the potential for use as memory elements in high density 1T-1C nonvolatile memories [2].

$CaBi_2Nb_2O_9$ (CBN) is a member of Bi-based layer-structured perovskite compounds [3] such as $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2TaNb_2O_9$ (SBTN) for which there has been a huge amount of research on nonvolatile random access memory applications [4]. Compared with SBT and SBNT thin films, there has been little reported on electrical properties of CBN thin films. Since the *c*-axis oriented CBN thin film had a low dielectric constant, it was considered to be a good candidate for application to nonvolatile ferroelectric memories. So far, the ferroelectric properties of CBN thin films have not been reported. CBN is a layered perovskite ferroelectric oxide, whose lattice constants are: $a = 50.5435$ nm, $b = 50.54658$ nm and $c = 52.4970$ nm [5]. For device applications, a single crystalline film has an edge over a polycrystalline film in obtaining stable and desirable properties. To obtain a good ferroelectric memory device exploiting ferroelectric film, it is required that the ferroelectric films have good ferroelectric properties, low interface state density, high breakdown strength and low leakage current. Usually, metal–ferroelectric-semiconductor is the desired configuration for a one transistor high density memory array for applications to nonvolatile memories. In this configuration, it is required the direct deposition of ferroelectric thin film on Si wafer. However, it is difficult to preserve ferroelectricity on Si due to existence of interfacial traps and/or interdiffusion of the constituent elements. Therefore, it is interesting to evaluate the ferroelectric properties of these films on metal electrodes such as platinum.

In previous works, our group has reported the preparation of thin films by the polymeric precursor method [6]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [7]. The precursor film is deposited by dip or spin-coating and then treated to eliminate the organic material and synthesize the desired phase. The polymeric precursor method presents many advantages, such as the possibility

* Corresponding author.
E-mail address: miganr@kenter.com (M.A. Ramírez).

0254-0584/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2005.09.004

to work in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipments).

Considering that the literature reports no data about the preparation of $CaBi_2Nb_2O_9$ (CBN) films through a polymeric precursor method, in this work, we describe our preliminary results on the deposition of thin films and their electrical properties relating to ferroelectric random access memory applications.

2. Experimental procedures

Calcium citrate (Synth), niobium oxide (Aldrich) and bismuth oxide (Aldrich) were used as raw materials. The precursor solutions of calcium, bismuth and niobium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of Ca, Bi and Nb solutions were mixed and homogeneized by stirring at 90 °C. The molar ratio of metal:citric acid:ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 12 cP by controlling the water content using a Brookfield viscosimeter. The CBN thin films were spin coated on $Pt/Ti/SiO_2/Si$ substrates by a commercial spinner operating at 5000 revolutions per minute for 30 s (spin coater KW-4B, Chemat Technology). In this work, an excess of 5 wt% of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as was reported in literature [8]. The thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness values of about 320 nm for CBN, reached by repeating the spin-coating and heating treatment cycles. The thickness of the annealed films was studied using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case, back scattering electrons were used. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu Kα radiation. The morphology of the thin films were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) by using a silicium nitride tip in the contact mode. AFM was used to obtain a three-dimensional image reconstruction of the sample's surface. These images allow for an accurate analysis of the sample's surface and the quantification of very important parameters such as roughness and grain size. The scan area was 1 m × 1 m in the *x–y* plane. For electrical measurements, a 0.5 mm diameter top Au electrode were deposited by evaporation through a shadow mask at room temperature. The electric properties were measured by an $Au/CBN/Pt/Ti/SiO_2/Si$ (1 0 0) capacitor structure. The capacitance–voltage (*C–V*) characteristic was measured in the metal–ferroelectric-metal (MFM) configuration using a small alternate current (ac) signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the direct current (dc) was swept from positive to negative bias. The relative dielectric constant ε_r were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). *J–E* characteristics of the films were measured using a Radiant Technology RT6000 A in a virtual ground mode at room temperature. A contact with probe electrodes was made with a wire-bonding method. Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology RT6000 A). For the fatigue measurements, internally generated 8.6 s wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies.

3. Results and discussion

Fig. 1 shows the XRD pattern of the 700 °C crystallized CBN thin film on platinum coated silicon substrate. The annealed thin film was a single phase of a layer-structured perovskite with orthorhombic crystallographic structure. The peaks were indexed according to following ref. [9]. The thin film showed random orientation with the highest intensity peak at $2\theta = 29°$. The main peak is very sharp, suggesting the presence of large crystalline grains in the film. Characteristic peak for platinum coated silicon (1 1 1) substrates was observed in the range of $38° < 2\theta < 41°$.

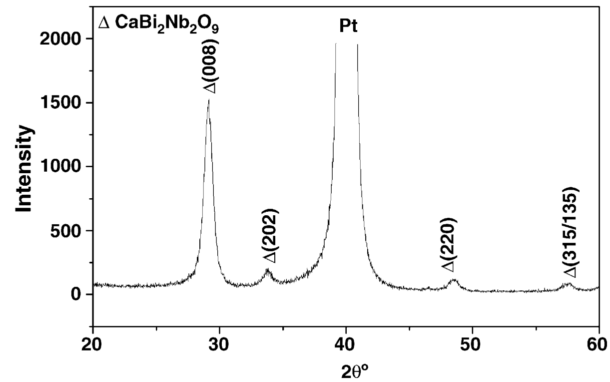

Fig. 1. X ray diffraction for CBN thin film annealed at 700 °C for 2 h.

Fig. 2 shows the typical AFM micrograph of the CBN thin film annealed at 700 °C for 2 h. Average grain size and surface roughness were estimated using a contact mode. The obtained morphology is crack free and of small porosity. The average surface roughness value is 16 nm while the average grain size consisting of isotropic round shape is 120 nm. This parameter roughness is extremely important since the dielectric properties depend not only on a well-defined microstructure but also of the relationship between the electrode interface-film. The morphology consists of large and small grains distributed along the films surface. The large grains was flat and their sizes was slightly smaller than the film thickness, implying that the growth behavior of each large grain was not similar to an epitaxial growth.

Low leakage current density is another important parameter for memory device applications. Here, the measured logarithmic current density (log *J*) versus the voltage (*V*) is shown (Fig. 3). The CBN thin films exhibited good leakage current characteristics. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. This ohmic behaviour occurs in insulat-

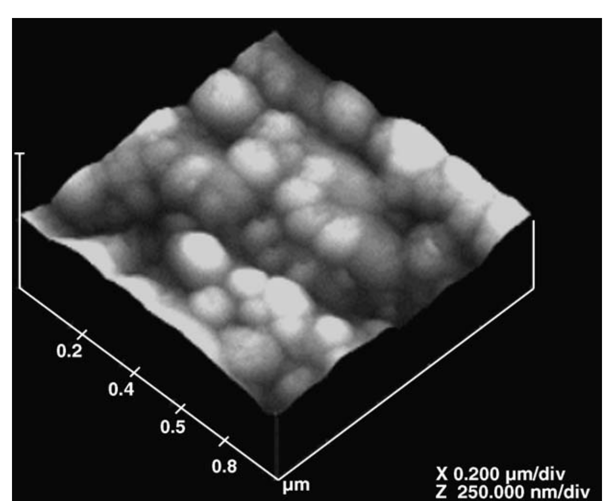

Fig. 2. AFM image for CBN thin film annealed at 700 °C for 2 h.

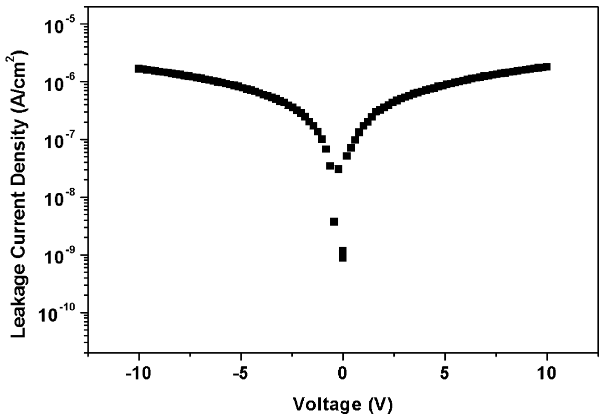

Fig. 3. Leakage current density in dependence of voltage for CBN thin film annealed at 700 °C for 2 h.

ing film as long as the film is quase neutral, that is, as long as the bulk generated current in the film exceeds the current due to injected free carriers from the electrode. This current would be due to the hopping conduction mechanism in a low electric field, because thermal excitation of trapped electrons from one trap site to another dominates the transport in the films. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanism. The leakage current density at 1.0 V is equal to 1.5×10^{-7} A cm^{-2} up to an applied electric field of 30 kV cm^{-1} establishing good insulating characteristics. It was noted a symmetric *J–V* characteristic for both voltage polarity indicating that the bulk controls the properties once we have used different top and bottom electrodes and having different processing conditions. Since the conductivity is strongly affected by the characteristics of the film–electrode interface, the surface morphology of CBN thin films is one of the major factors determining the leakage current in capacitors. The low leakage current value can be attributed to the small surface roughness as was observed in Fig. 2.

Fig. 4 illustrates the *C–V* curve for CBN films obtained at 100 kHz and dc sweep voltage from +10 to −10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The *C–V* curve for the film annealed at

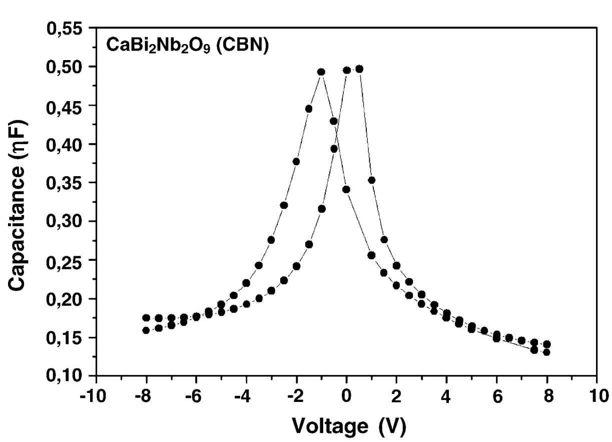

Fig. 4. *C–V* curve for CBN thin film annealed at 700 °C for 2 h.

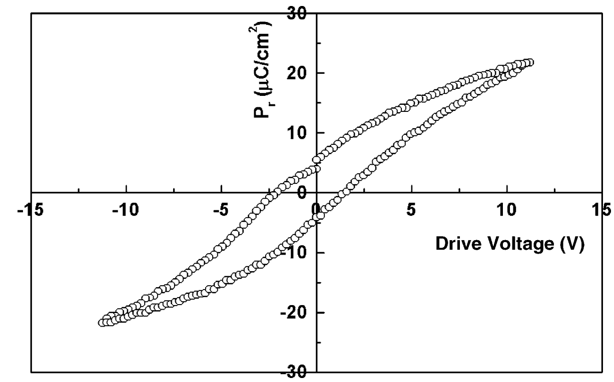

Fig. 5. *P–V* hysteresis loop for CBN thin film annealed at 700 °C for 2 h.

700 °C for 2 h also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The symmetry around the zero bias axis indicates that the films contain few movable ions or charge accumulation at the film–electrode interface. The dielectric constant of the CBN thin films calculated from C_{max} was 90. The dissipation factor was 0.053 at 100 kHz. Similar results were obtained by CBN films deposited on n(+)–Si(100) substrates by pulsed laser deposition [10]. Because the CBN thin film shown ferroelectric nature, hysteresis curve were examined at room temperature in MFM configuration (Fig. 5). Ferroelectricity of the calcium bismuth niobate was observed with remanent polarization (P_r) and a drive voltage V_c of 4.2 C cm^{-2} and 1.7 V, though the hysteresis loop was not fully saturated at the applied voltage. The low remanent polarization value can be related to the growth in *c*-axis direction, which is evident for bismuth-based layer-structured perovskite compounds [11]. New studies should be performed in order to understand the contribution of *c*-axis direction on the ferroelectric properties of this system. It can be also noted the absence of imprint which causes a significant shift along the electric field axis towards the positive side. This indicates that our films presents a small concentration of space charges in the electrode–film interface. These results are consistent with the *C–V* measurements where was observed symmetry around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film–electrode interface (Fig. 4).

Among the degradation processes in ferroelectric thin films, polarization fatigue has received the most attention especially in thin films deposited on platinum electrodes. The fatigue endurance of CBN thin films were tested at 1 MHz as a function of switching cycles by applying 8.6 s wide bipolar pulses with maximum amplitudes of ±10 V (Fig. 6). P^* is the switched polarization between two opposite polarity pulses and $\hat{P}$is the nonswitched polarization between the same two polarity pulses. The $P^* - P^\wedge$ or $-P^* - (-P^\wedge)$ denote the switchable polarization, which is an important variable for nonvolatile memory application. Fatigue resistance was observed up to 1×10^8 cycles suggesting that CBN has good potential for applications in memories. However, new studies should be performed aiming to understand its source and improve the fatigue resistance to higher cycles.

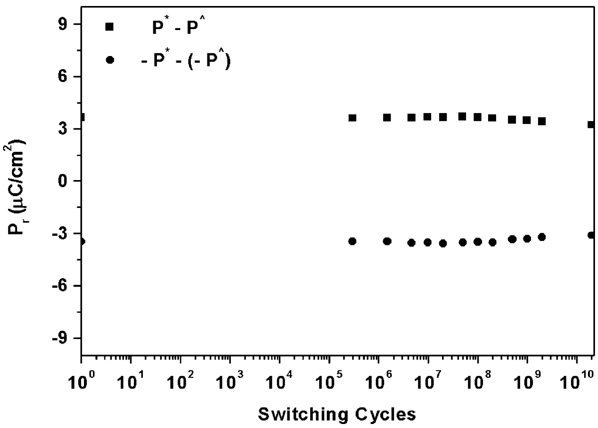

Fig. 6. Fatigue as a function of polarization cycles for CBN thin film annealed at 700 °C for 2 h.

4. Conclusions

Highly *c*-axis oriented $CaBi_2Nb_2O_9$ (CBN) thin films were successfully deposited directly on platinum coated silicon substrates by the polymeric precursor method. The CBN thin films exhibited good structural and a dense microstructure. The typical measured small signal dielectric constant and dissipation factor at 100 kHz were 90 and 0.053, respectively. The leakage current density was around 10^{-7} A cm^{-2} at an applied electric field of 30 kV cm^{-1}. The remanent polarization and the drive voltage values were 4.2 C cm^{-2} and 1.7 V, respectively. No significant fatigue was observed at least up to 10^8 switching cycles. The results of these studies are very promising and suggest that CBN thin films can be used as storage element in nonvolatile ferroelectric random access memories.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq and CAPES.

References

[1] S.B. Desu, R. Ramesh, B.A. Tuttle, R.E. Jones, I.K. Yoo (Eds.), Ferroelectric Thin Films V, vol. 433, 1996.
[2] S. Sinharoy, H. Buhay, D.R. Lampe, M.H. Francombe, J. Vac. Sci. Technol. A 10 (1992) 1554.
[3] G.A. Smolenskii, V.A. Bokov, V.A. Isupov, N.N. Krainik, R.E. Pasynkov, A.I. Sokolov, in: G.A. Smolenskii (Ed.), Ferroelectrics and Related Materials, Gordon and Breach Science Publishers, New York, 1984 (Chapter 15).
[4] C.A.P. Araujo, J.D. Cuchiaro, L.D. McMillian, M.C. Scott, J.F. Scott, Nature (London) 374 (1995) 627.
[5] G.V. Gibbs, M.B. Boisen Jr., R.T. Downs, K.L. Bartelmehs, XPOW-PLOT Version 2.0, 1993.
[6] A.Z. Simões, A. Ries, F.M. Filho, C.S. Riccardi, E. Longo, J.A. Varela, Appl. Phys. Lett. 85 (2004) 5962.
[7] A.Z. Simões, A.H. Gonzalez, C.S. Riccardi, M. Cantoni, M.A. Zaghete, B.D. Stojanovic, J.A. Varela, J. Eur. Ceram. Soc. 24 (2004) 1607.
[8] B.S. Kang, B.H. Park, S.D. Bu, S.H. Kang, T.W. Noh, Appl. Phys. Lett. 75 (1999) 2644.
[9] S.B. Desu, H.S. Cho, P.C. Joshi, Appl. Phys. Lett. 70 (1997) 1393.
[10] H.S. Cho, S.B. Desu, Phys. Status Solidi A, Appl. Res. 161 (1997) 371.
[11] M.-W. Chu, M. Ganne, M.T. Caldes, L. Brohan, J. Appl. Phys. 91 (2002) 3178.