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Mechanical Properties of Ferroelectric Composite Thin Films Fabricated by the Pulsed Laser Deposition Method

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Abstract

Barium strontium titanium oxide (BSTO) ferroelectric films of various nominal thicknesses were deposited by the pulsed laser deposition (PLD) technique on single crystals of sapphire at substrate temperatures varying from 30° C to 700° C. X-ray analysis showed that the thin films were amorphous up to 500° C, while at 700° C, they were polycrystalline. The microstructure of the thin films was columnar at all substrate temperatures. The film microhardness increased with increasing substrate temperature. While the cohesion failure load of the films remained fairly constant, the adhesion failure load increased with increasing substrate temperature.

Table of Contents

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List of Figures

List of Tables

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1. Introduction

The concept of electronic thin film deposition at lower temperatures is desirable because it enables the integration of several device fabrication steps. However, the inherent material properties required for any application have to be maintained at the lower deposition temperatures. In the case of electronic thin films used for tunable dielectric applications, these properties include dielectric constant, voltage tunability, and the electronic loss tangent. However, the mechanical integrity of the thin film (i.e., the adhesion and cohesion) is just as important.

It is well known that the substrate temperature T_s, the ambient gas pressure, and the energy of any incoming ions influence the growth conditions and, therefore, the film structure produced under low-pressure conditions (Movchan and Demchishin 1969; Thornton 1977; Fountzoulas and Nowak 1991). A structural classification system that has gained the broad acceptance for thin films produced by the physical vapor deposition (PVD) process has been presented by Movchan and Demchishin (1969). They proposed three zones to describe the microstructures that can develop in deposits produced by vacuum evaporation as a function of T_s/T_m, where T_s is the absolute substrate temperature and T_m is the absolute melting temperature of the deposited material. Thornton (1977) elaborated on the approach of Movchan and Demchishin, extending it to typical sputtering conditions. Thornton also concluded that the structure and physical properties of films produced by sputtering could be represented as a function of T_s/T_m, in terms of four zones as shown in Figure 1, each with its own characteristic structure and physical properties. The general features of Thornton's model were based on the examination of 25- to 250-μm-thick coatings deposited at argon pressures 1.33×10^{-4} (1 mTorr) to 3.9×10^{-3} Pa (30 mTorr) using cylindrical-post and hollow cathode magnetron sputtering sources. Fountzoulas and Nowak (1991) further elaborated on the approach of Movchan and Thornton, extending it to ion plating.

We have initiated an investigation of the cohesive and adhesive properties of dielectric thin films of barium strontium titanium oxide (BSTO) deposited on single crystal substrates by the pulsed laser deposition (PLD) method (Sengupta et al. 1996; Brennan 1992; Lee, Ramesh, and Keramidas 1995).

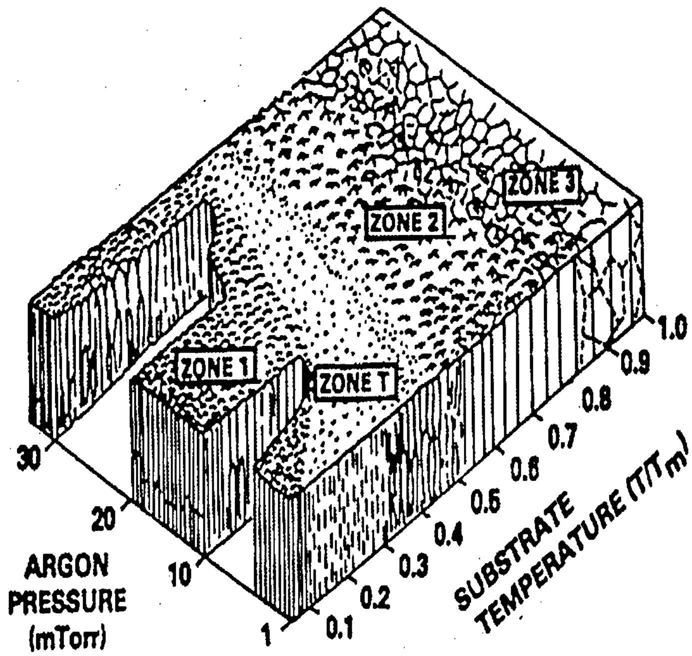

Figure 1. Thornton's Structure Zone Model for Coatings Produced by Sputtering (Thornton 1977).

This report presents the initial results of this study of these mechanical properties of BSTO thin films as a function of deposition temperature.

2. Experimental Procedure

In this work, thin films of BSTO were deposited by the PLD technique on single crystal sapphire substrates at room temperatures varying from 30° C to 700° C. The details of this deposition technique are given in Sengupta and Green (1998).

The fracture cross sections of the films were observed by scanning electron microscopy (SEM). Crystallinity, crystal orientation, and composition of the films were determined by FT-RAMAN spectroscopy and glancing angle x-ray diffraction (GAXRD). The adhesive and cohesive failure loads of the films were evaluated with the aid of a CSEM-Revetest instrument (Centre Suisse d' Electronique et de Microtechnique, CSEM, CH-20007, Neuchâtel, Switzerland).

In the specimen evaluation, the material properties of the BSTO thin films deposited at various substrate temperatures were evaluated by FT-Raman spectroscopy (Sengupta and Green 1998).

The Knoop microhardness of the coatings, uncorrected for substrate hardness effects, was measured using a 0.25-N applied load and a dwell time of 15 s. Even at this low load, the maximum indenter penetration far exceeded the critical value of 1/10 of the coating thickness considered sufficient for the substrate not to have a significant effect on hardness values.

The cohesion and adhesion values of the various coatings were evaluated primarily with a CSEM-Revetest automatic scratch apparatus. This apparatus, with a diamond stylus radius of 20 µm, and the testing procedure are described in Kattamis et al. (1993); Bhansali and Kattamis (1990); Kattamis (1993); and Steinmann, Tardy, and Hintermann (1987). The sample translation speed was held constant at 5 mm/min, and the loading rate at 5 N/min; hence, the load gradient was $dL/dx = 1$ N/mm. The cohesion failure load (L_C) is the minimum crack initiation load within the coating, and the adhesion failure load (L_A) is the minimum load at which the crack causes massive delamination at the coating/substrate interface.

3. Results and Discussion

3.1 SEM Analysis. The microstructure of the BSTO thin film, at various substrate temperatures, was evaluated by SEM photomicrographs (Figure 2). It became apparent from the SEM photomicrographs that the Thornton structural zone 1 (Thornton 1977) was not observed. Our films can be classified in the Thornton transition (T) and structural zone 2. The column size measurements as a function of the ratio of the absolute substrate temperature (T_s) and absolute film melting temperature (T_m) (2,004 K) are shown in Table 1 and Figure 3. For T_s/T_m between 0.15 and 0.19, the average column size increased from 190 nm to 230 nm. For T_s/T_m between 0.19 and 0.39,

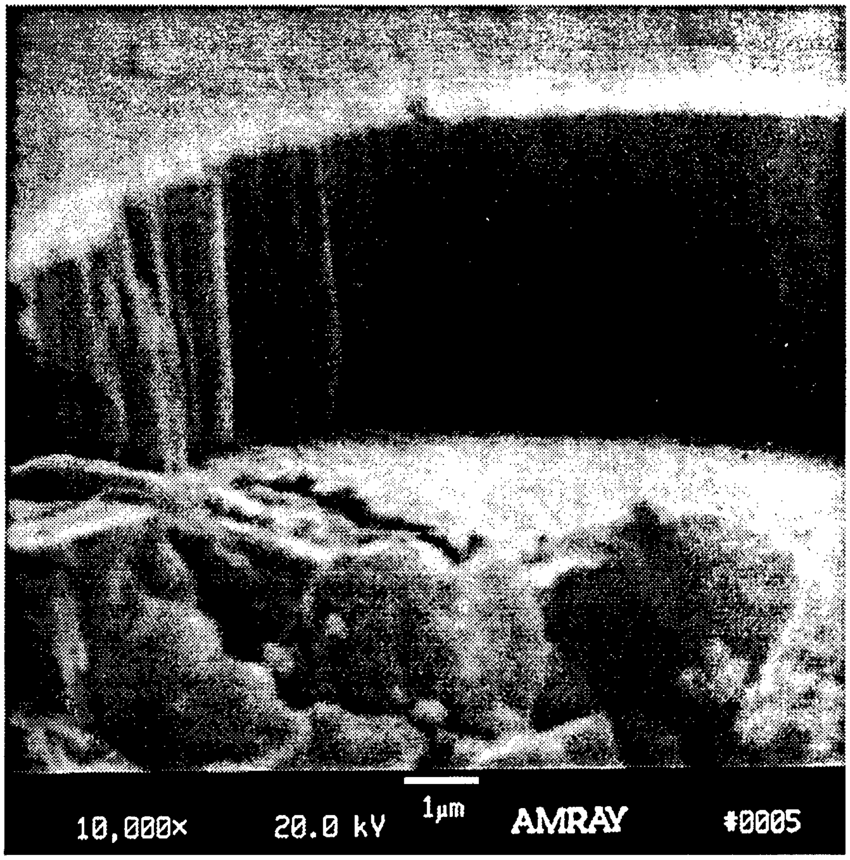

Figure 2. SEM Photomicrograph of Fracture Cross Section of a BSTO Film ($T_s / T_m = 0.15$).

Table 1. Column Size, Cohesion and Adhesion Failure Load, and Knoop Microhardness of BSTO Films vs. T_s / T_m

T_s / T_m	Thickness (nm)	Column Size (nm)	L_C (Cohesion Load) (N)	L_A (Adhesion Load) (N)	Knoop Microhardness (GPa)
0.15	1,000	190	11.63	16.06	1.3
0.19	2,200	230	13.75	18.75	1.5
0.29	1,000	250	13.65	38.22	5.7
0.39	1,000	220	12.96	22.68	6.6
0.49	3,000	2,007	12.32	24.08	7.0

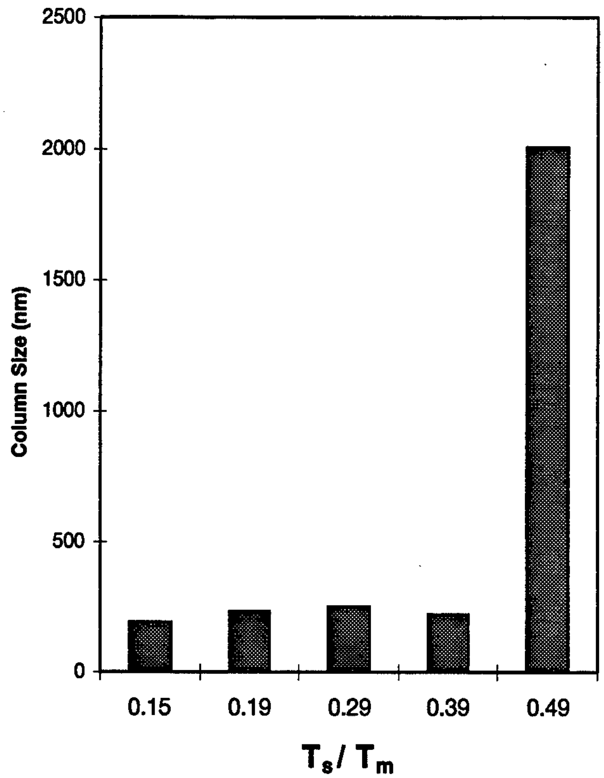

Figure 3. Column Size of BSTO Films vs. T_s / T_m.

the average column size remains practically constant. At T_s /T_m = 0.49, where the film is fully crystalline, the column size increases dramatically to 2,007 nm.

3.2 Microhardness. The Knoop microhardness of the BSTO films, uncorrected for the substrate hardness effect, ranged between 1.3 GPa and 7 GPa. Table 1 and Figure 4 show Knoop microhardness values as a function of T_s /T_m. The film microhardness increased with increasing T_s / T_m ratio and increasing film crystallinity. The highest Knoop microhardness was obtained at the highest temperature (T_s /T_m = 0.49).

3.3 Cohesion and Adhesion Failure Load. Measured average values of cohesion failure load (L_C) and adhesion failure load (L_A) are listed in Table 1. The cohesion failure load of the films remained fairly constant, independent of the substrate temperature (Figure 5). The average cohesion failure load of the film was about 13 N. The adhesion failure load of the films increased with

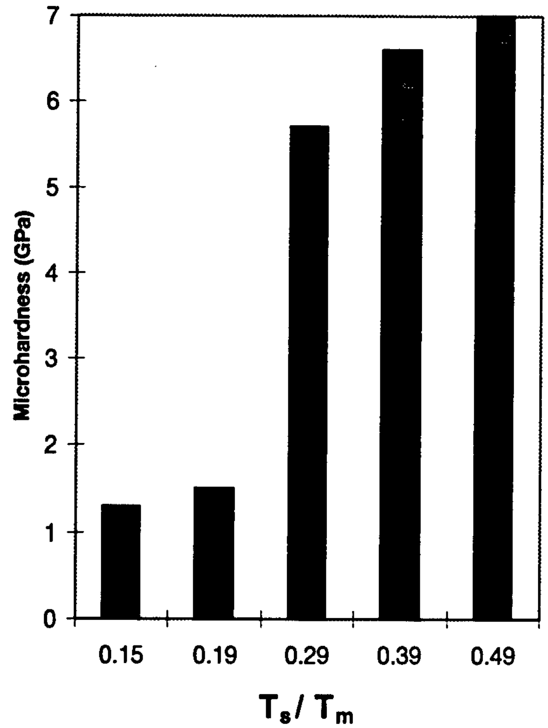

Figure 4. Knoop Microhardness of BSTO Films vs. T_s / T_m.

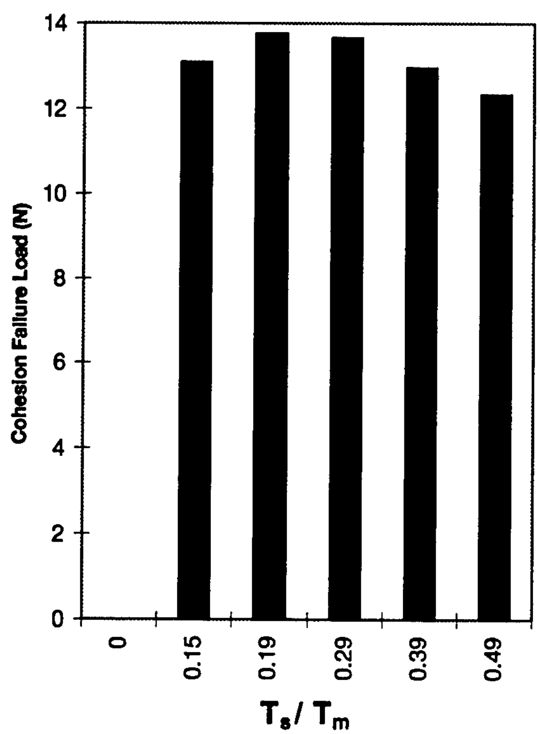

Figure 5. Cohesion Failure Load of BSTO Films vs. T_s / T_m.

increasing T_s/T_m ratio (Figure 6). However, for reasons currently not understood, for $T_s/T_m = 0.25$, the adhesion failure load exhibited a peak at a ratio of 0.29.

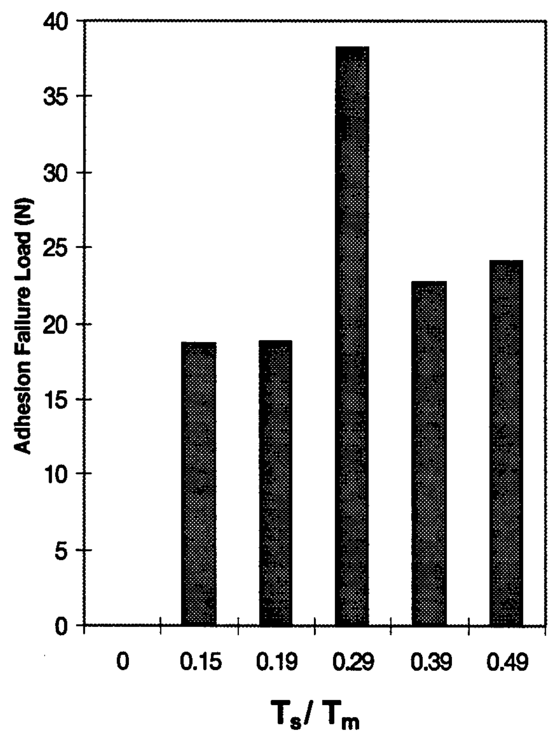

Figure 6. Adhesion Failure Load of BSTO Films vs. T_s/T_m.

4. Conclusions

The structure, crystallinity, cohesion and adhesion failure loads, and microhardness of BSTO thin films produced by PLD were correlated with the substrate temperature. For the entire temperature range, 278–973 K, the films were columnar and the column size increased with increasing substrate temperature. For $T_s/T_m \leq 0.29$, they could be categorized as being in the transition (T) Thornton structural zone, while for $T_s/T_m > 0.29$, they corresponded to the Thornton structural zone 2 category. The film was amorphous up to 373 K, partially crystalline from 573 to 973 K, and fully crystalline at 973 K. The cohesion failure load was constant for the entire substrate temperature range. The adhesion failure load and microhardness increased with increasing thin film crystallinity and substrate temperature.

5. Future Plans

The microstructure evolution of the BSTO films as a function of the substrate temperature, laser pulse energy, and oxygen pressure will be further studied in order to construct a more comprehensive structure zone model for PLD BSTO films produced by the technique.

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