PREPARATION AND PROPERTIES OF THIN FILM MATERIALS WITH PEROVSKITE TYPE STRUCTURE (MIXED OXIDES ABO3)

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PREPARATION AND PROPERTIES OF THIN FILM MATERIALS WITH PEROVSKITE TYPE STRUCTURE (MIXED OXIDES ABO₃)

Abstract. — Barium Titanate (BaTiO₃) and Lithium Niobate (LiNbO₃) thin films (0.2 to 1 μm) were deposited onto Platinum foils and Silicon wafers (M. I. S. capacitor structure). In the present work, polycrystalline films which had been prepared by R. F. cathodic sputtering of ceramic targets were studied. With a substrate temperature below 300 °C during the deposition, good insulating amorphous films with a low dielectric constant were obtained, but with a postdeposition heat treatment (~ 600 °C) the deposits show some ferroelectric properties (high dielectric constant, non-linearity, etc.). However, the magnitude of the phenomena is still small and difficult to control, but these encouraging results justify a continuation of the study.

I. Introduction. — During the last decade, various methods have been investigated to prepare thin films of high permittivity materials for application in microelectronic circuits, as a passive element (high value capacitors), or as active elements in the M. I. S. (Metal-Insulator-Semiconductor) structure. More recently the need of materials with electro-optical properties, for applications in optical display systems and optical memories, gave a new impetus to the study of thin ferroelectric films and particularly the materials with perovskite type structure (mixed oxides ABO₃).

A review of methods for depositing ferroelectric thin films has been published by Feuersanger [1]. Our efforts in this field have been concentrated on Barium Titanate (BaTiO₃) [2]-[3] and Lithium Niobate (LiNbO₃).

II. Sputtering techniques and equipment. — The R. F. sputtering system set up followed a conventional diode design. The vacuum system consisted of a Balzers high vacuum pumping unit PST 1900 A automatically controlled, including an oil diffusion pump (2 000 l/s) with multi-coolant baffle for water or nitrogen cooling. The sputtering module was built around a multi-cathode SP 430 — Mathis module. The main specifications are:

- 3 ø 90 mm electrodes cooled by water.
- The low pressure limit at the top of the chamber : 1 x 10⁻⁷ torr.
- Magnetic field : 0-100 G.
- R. F. generator : 13.56 MHz : 0-1 000 W.
- Gas supply : argon and oxygen commercially available 5/9 are introduced into the system through stainless tubing and controlled by a needle valve; automatically controlled or not (as a function of pressure).
- Targets : the targets are pressed and sintered in our ceramic Laboratory, according to classical techniques, from very high purity powders.
- Substrates : various materials have been utilized as substrates. Among these, diamond polished platinum, quartz, and silicon wafers are found. The latter has been mainly used for studying M. I. S. capacitors structures.
TABLE I
Sputtering conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. F. Power during deposition</td>
<td>0.5 to 1.5 W/cm² (target)</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>40 G</td>
</tr>
<tr>
<td>Total discharge pressure</td>
<td>1 to 5 millitorr</td>
</tr>
<tr>
<td>Oxygen concentration</td>
<td>0% (residual) or 100%</td>
</tr>
<tr>
<td>Argon concentration</td>
<td>0% or 100%</td>
</tr>
<tr>
<td>Anode-cathode spacing</td>
<td>5 cm</td>
</tr>
<tr>
<td>Deposit bias</td>
<td>floating (~ -50 V)</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>20 to 70 Å/m²</td>
</tr>
</tbody>
</table>

III. Films properties. — The thickness of the thin films is of the order of 0.2 to 1 μm, they are transparent, and adhere very well to the substrates. Their properties depend on the deposition parameters, the main factors determining the properties of the perovskite films are: substrate temperature, oxygen partial pressure, deposition rate. For the moment, we cannot control oxygen partial pressure, during sputtering, it is equal to, either the residual oxygen pressure in the chamber (noted 0 %) or 100 % of the total discharge pressure. With 0 % of oxygen, the BaTiO₃ target remains uncharged (no reduction) after several hours of ion bombardment and the films present some beautiful interference colors. However, with the same conditions, the LiNbO₃ films have a dark brown color, almost metallic in appearance. And in order to have a transparent film we have worked up to now at 100 % oxygen.

The crystallographic studies as well as the leakage current at high field have shown that the BaTiO₃ films had a slight oxygen deficiency, and LiNbO₃ films an excess. In the two cases, the films have some semiconductive properties.

In the future, we shall use a mass spectrometer which will monitor oxygen introduction during sputtering.

Electrical studies of the M. I. S. capacitance versus bias and measurement frequency yield informations about the evolution of the charges in the films, and the coupling of the ferroelectric and semiconductor properties.

BaTiO₃ Films characteristics. — Immediately after deposition of the films on cooled substrates (surface temperature ~ 300 °C) there are amorphous and do not show ferroelectric properties (er ~ 20).

A post-deposition heat treatment at 600 °C to 700 °C (1-2 hours) in an oxygen atmosphere was necessary to obtain the following characteristics: dielectric constant εr on platinum is of the order of 100 to 350, on silicon, the measured values are lower (50 to 150) — due to a thin parasitic SiO₂ film between BaTiO₃ and the silicon wafer. The dissipation factor tg δ at 1 KHz varied from 0.02 to 0.08. The breakdown field is of the order of 5 x 10⁵ V/cm.

The current-field dependence is ohmic ρ ~ 10⁹ to 10¹¹ Ω.cm for low electric fields, and non-ohmic (~ exponential) and asymmetric in the Pt-BaTiO₃-Al structure for high field > 1 x 10⁵ V/cm. Differences of several orders of magnitude in DC conductivity were encountered among various samples. Our best samples gave a high dependence of the dielectric constant on field strength, a variation of ΔC/С ≈ 45% for a variation of the electric field from 0 to 6 x 10⁵ V/cm (Fig. 1).

Fig. 1. — Dependence of the dielectric constant on field strength at room temperature. Structure: Pt-BaTiO₃-Al; Reference: Pt 4 BaTiO₃ thickness = 5700 Å; Heat treatment: T = 600 °C (1 hour).

Fig. 2. — Dependence of the M. I. S. capacitance with a ferroelectric insulator versus electric field at room temperature. Structure: Si(N: 0.05 Ω.cm)-BaTiO₃-Al; Reference: SF Al8 C-BaTiO₃ thickness = 5400 Å; Heat treatment: T = 660 °C (1 hour).

Deposits on silicon show coupling of non-linearity properties of the dielectric constant versus electric field in the positive voltage area on figure 2, and the silicon surface properties in the negative voltage area,
since silicon is of N type conductivity. X rays analyses show that ferroelectric and paraelectric states coexist in the films at room temperature, with, however, a predominancy of the cubic phase.

It was not possible to change this structure by means of heat treatments ($T < 900 \, ^\circ C$).

**LiNbO$_3$ Films Characteristics.** — Our first films deposited in pure oxygen (100 %) have given encouraging results; the films are insulating and transparent.

The dielectric constant is of the order of 80 to 100, the dielectric losses are however rather high 8-30 %.

The crystallographic studies by electron diffraction showed a cubic structure. The 100 % oxygen atmosphere seems to have led to a deposit of mixed oxides rich in oxygen whose composition is in process of analysis.

The optical, electro-optical, piezoelectric and elasto-optical properties of these films are studied in our coherent optics laboratory.

**IV. Conclusion.** — The deposits show some ferroelectric characteristics (high dielectric constant, non linearity, etc.). The magnitude of the phenomena are still small and difficult to control. However, we feel that the way chosen for the realization of these complex structures is adequate and is continually improving, as has been shown by Westinghouse [4] and I. B. M. [5] recent work.

In particular, the recent use of substrate-tuning methods [6] in a R. F. discharge, and the monitoring of the reactive gas with a mass spectrometer during film growth, should allow a much better control of structure and composition of thin films.

Our current efforts are aimed in this direction.

**References**


