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SOL-GEL PROCESSED $BaTiO_3$

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ABSTRACT

$BaTiO_3$ thin films deposited on pyrex supports by dip-coating technique and powders have been prepared by the sol-gel route from sols containing a mixture of tetraisopropyl orthotitanate, iso propanol, barium acetate and glacial acetic acid. The thickness of the films is proportional to the first power of the withdrawal speed. Gelled sols have been dried hypercritically and by natural evaporation. Films and powders have been characterized by X-ray diffraction during their heat treatment. Tetragonal $BaTiO_3$ structure is observed for $T \geq 600°C$.

INTRODUCTION

The deposition of thin films on glass, ceramic and metal substrates is one of the most important application of the sol-gel process. The dip-coating technique consists in dipping a clean substrate in an organometallic solution and lifting it at a constant speed. During this process thin liquid films stick on the two faces of the substrate; they hydrolyse rapidly with the air humidity and polycondensate. After drying, these layers are usually porous but can be easily densified at relatively low temperature. Their thickness depends on the lifting speed (v), the sol viscosity (η), density (d) and surface tension (σ) and the temperature of the heat treatment.

After a certain time, the sols usually transform into a humid gel which can be dried by natural evaporation (xerogel) or by hypercritical solvent evacuation (aerogel). After subsequent heat treatment these porous materials can be either densified into a monolithic product or transform into crystalline powders which can be later processed to obtain ceramics of well characterized properties.

In this paper we present results concerning the preparation of $BaTiO_3$ thin films and powders by the sol-gel route and their characterization by an optical technique, X-ray diffraction and optical microscopy.

RESULTS AND DISCUSSION

Sols have been prepared by diluting 2,7ml of tetraisopropyl ortho-titanate in 47ml of isopropanol under strong agitation at room temperature during 30 minutes. Then 2.38g of barium acetate with mole ratio $[Ba] / [Ti] = 1$ diluted in 6ml of water is added slowly under continuous stirring. In order to avoid precipitation and to maintain a stable viscosity for a certain time we also added a few drops of acetylacetone and acetic acid . The sol was kept then under vigorous stirring for two more hours.

Thin films of optical quality can be deposited with a lifting speed of 6 to 20mm/min if the viscosity is kept between 2.5 and 4.0 cp. The porous films can be densified by heating in air at 600°C for 5 min. The films are homogeneous and transparent with an index of refraction $\eta = 2.10 \pm 0.05$ at 550nm in agreement with Yanovskaya [1] (the literature gives a value of 2.4 for $BaTiO_3$ single crystals). Their thickness varies linearly with the speed. The process can be repeated several times in order to increase the thickness of the layers (Figure 1). For $BaTiO_3$ concentration larger than 20g/l the dense films are no longer homogeneous and cracks are

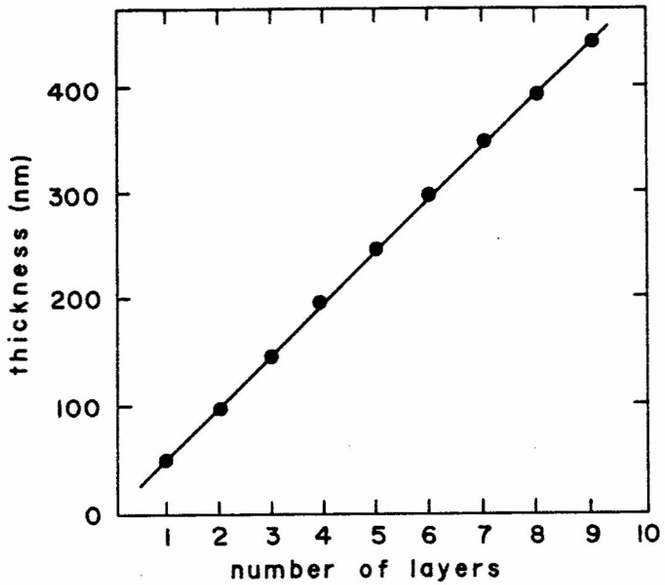

Figure 1 - Variation of thickness of the layer as a function of the number of coating v=10mm / min, η = 3.1 cp.

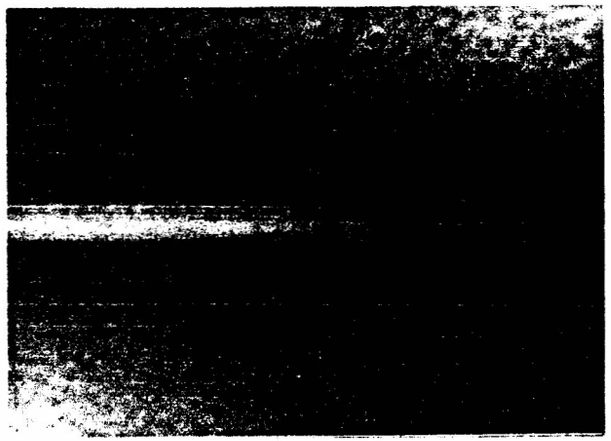

Figure 2 - SEM micrograph of a $BaTiO_3$ thin film deposited on a pyrex support after 600°C heat treatment; the bar on the lower right side corresponds to 13nm.

observed.

Figure 2 is a scanning electron microscope micrograph of a typical $BaTiO_3$ thin film densified at 600°C. Its grain structure is quite fine and regular without cracks and defects The films are highly adherent to the glass support. When deposited on a teflon substrate they are easily removed and their structure can therefore be studied by X-ray diffraction as a function of the temperature of the heat treatment. Up to 550°C the films are totally amorphous; they crystallize already around 600°C into a tetragonal $BaTiO_3$ structure (figure 3).

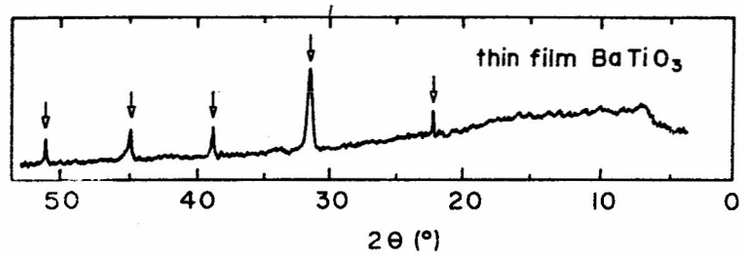

Figure 3 - X-ray diffraction of thin film sol-gel $BaTiO_3$ heat treated at 600°C. The back-ground at low angle is partly due to the support. The arrows indicate the position of X-ray lines oi tetragonal $BaTiO_3$.

These sols gel typically after a few days and transform into white opaque humid gel; they can be dried either by hypercritical solvent evaporation in an autoclave under 280°C and 200 bar with the formation of white needles (Figure 4) or by normal evaporation at room temperature (xerogel) with the formation of structureless white powder.

Figure 4 - White needles obtained after hypercritical solvent evaporation measured with an optical microscope.

The crystalline structure of these needles is shown in figure 5 measured just after the hypercritical solvent evaporation and after a heat treatment in air at 600°C during 10 minutes.

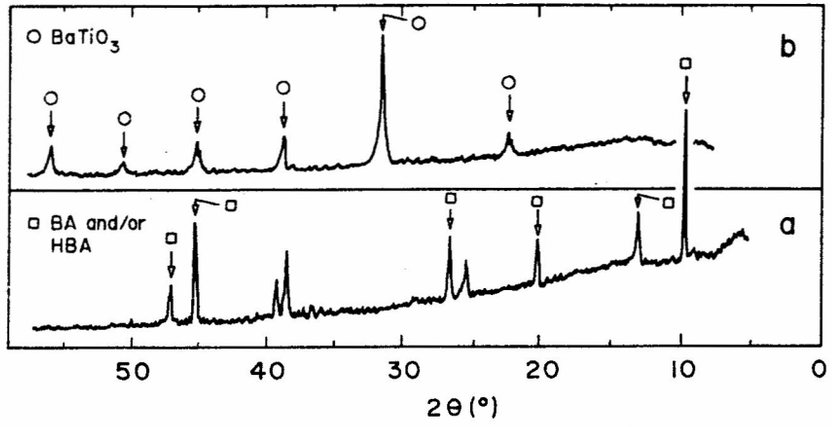

Figure 5 - X-ray diffraction of the $BaTiO_3$ needles measured : a) after the hypercritical solvent evaporation b) after a heat treatment in air at 600°C during 10 minutes.The arrows indicate the formation of X-ray lines of $BaTiO_3$, barium acetate and hydrated barium acetate.

In the first case (a) the needles appear partly amorphous with a superposition of X-ray lines which are attributed to barium acetate (BA) and to hydrated barium acetate (HBA). The rest of the lines are still unknown. After a 10 min 600°C heat treatment the films crystallize in a tetragonal $BaTiO_3$ structure (b). The same structure has been obtained for the white powder heat treated at the same temperature.

In conclusion we showed that it is possible to prepare thin films and powder of $BaTiO_3$ from the sol gel route using a mixture of Ti alkoxide and Ba acetate. Measurements of the dielectric properties are underway.

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MOLECULAR BUILDING BLOCKS IN LOW PH SILICON SOL-GELS: A SILICON-29 NMR STUDY

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ABSTRACT

High field Silicon-29 NMR is used to study the structural intermediates in tetramethyl and tetraethyl orthosilicate (TMOS and TEOS) low pH sol-gel reactions. Linear oligomers as well as ring components of various sizes are identified and their evolution in the sols is followed. Differences in the number of compact ring structures are related to differences in gel times. Reactions are followed for various silicon alkoxide:water:acid molar ratios.

INTRODUCTION

The use of proton NMR [1] and Silicon-29 NMR [2] has provided valuable information on the hydrolysis and polymerization reactions in sol-gel systems. Silicon-29 NMR is now used to identify reacting chemical species in selected tetramethyl and tetraethyl orthosilicate (TMOS and TEOS) sols. The concentrations of these oligomeric molecular building blocks are determined and early growth of the polymer followed. New high field (99.36 MHz) Silicon-29 NMR assignments allow us to follow structural variations into very large polymers.

TEOS and silicon sols with larger alkoxide groups, when reacted under identical conditions, take over twice as long to gel as TMOS sols. These differences are not simply related to hydrolysis or condensation kinetics. However, a correlation can be made between the molecular building blocks of the polymers and their gel times. These differences should be related to variations in material properties as well.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of a TMOS (a) and TEOS (b) sol 2 h after water and acid were added. The spectra for reactions using tetrapropyl orthosilicate (TPOS) and larger alkoxides are similar to TEOS.

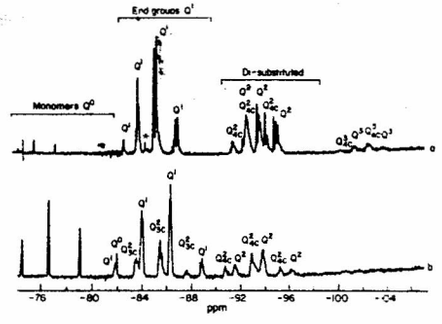

Fig. 1. Silicon-29 NMR spectra of (A) TMOS + MeOH and (B) TEOS + EtOH at t_0 + 2 h with a silicon:water:acid ratio of 1:2:0.02. Note the presence of ring compounds (Q_{3C}) in TEOS compared to TMOS within the end group region.

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