

Crystallization behaviour of barium titanate thin films

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Abstract

Barium titanate thin films were prepared by a sol-gel route on alumina and single crystal silicon substrates. The crystallization behaviour in dependence on substrate material and heat treatment was characterized by X-ray diffraction and infrared spectroscopy. Remarkable differences between these two substrate materials were found and could be attributed to chemical surface properties.

1. INTRODUCTION

Many applications in the field of ferroelectric materials require the use of thin films. Typical examples range from thin film capacitors to complex memory and electro-optical devices. At present ferroelectric prototype memories are produced either by sputtering or by sol-gel techniques [1]. One possible candidate for these applications is BaTiO_3 because it exhibits strong ferroelectric properties.

The deposition of thin barium titanate films by sol-gel techniques on various substrates has been reported in [2-6]. These high purity films crystallize between 600 and 700°C to tetragonal BaTiO_3 and exhibit a fine-grained microstructure. Ferroelectric properties are obtained after annealing of the films above 700°C for a certain period of time [6]. But up to now the influence of the substrate on the crystallization behaviour of sol-gel derived barium titanate films has not been investigated. Recently it was found by Lee and Park [7] that films deposited by metal organic chemical vapour deposition have a low dielectric constant which was attributed to crystalline impurities. From this point of view the goal of this work was to investigate the influence of substrate on the crystallization behaviour of sol-gel derived barium titanate films as a function of temperature.

2. EXPERIMENTAL

Fig. 1 shows the flow diagram of the film preparation. An alkoxide-hydroxide route was used as previously proposed by Kiss et al. [8]. Hydrated barium hydroxide is dissolved in ethanol and acetic acid. Then an equimolar amount of titanium ethoxide was added. The reactions that take place during this process are described in [9]. A homogeneous sol

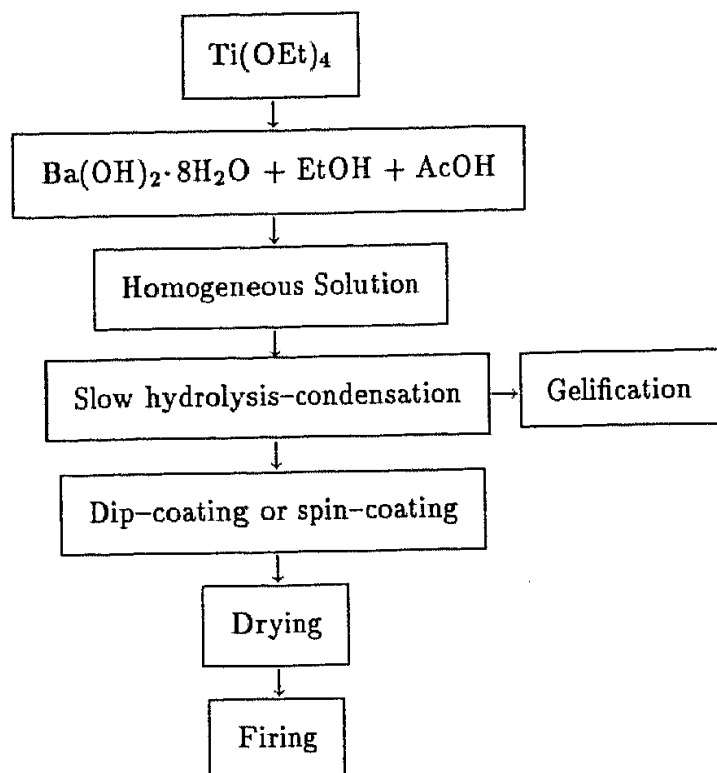


Figure 1. Film preparation.

was obtained and gelification leads to a monolithic gel after a few days.

The careful control of the rheological properties of the organometallic solution allows the deposition of homogeneous and crack-free films onto silicon and alumina substrate by spin-coating and dip-coating technique [10]. After drying at 110°C the films were fired at different temperatures in the range between 600 and 900°C for 2 h in ambient atmosphere.

The film thickness was measured by ellipsometry. A thickness of $0.2 \mu\text{m}$ after heat treatment was achieved by one coating step. Thicker films were obtained by repetition of the coating steps.

X-ray structural analysis was carried out with a Siemens diffractometer (D 500) using $\text{CuK}\alpha$ radiation. The infrared absorption spectra of the films on silicon were measured in the range from 200 to 1600 cm^{-1} using a Perkin-Elmer spectrometer. Reference data were taken from uncoated and not heat-treated silicon wafers.

3. RESULTS AND DISCUSSION

In a previous work about powder synthesis by the same chemical route it was shown that differential thermal analysis of the dried gels exhibits an exothermic peak at 680°C , which was attributed to the crystallization of the BaTiO_3 perovskite structure [11].

The X-ray diffraction spectra of films on alumina and silicon substrates as a function of calcination temperature are presented in Fig. 2 and 3, respectively. All diffraction patterns can be correlated to the films and the substrate materials. The crystallite size of the BaTiO_3 films after heat treatment at different temperatures was calculated from the line width of the (111) reflection by using the approximation method [12]. The results are summarized in table 1.

The crystallite size just after the crystallization of BaTiO_3 ranges from 170 nm (silicon, 680°C) to 190 nm ($\alpha\text{-Al}_2\text{O}_3$, 630°C) and crystal growth occurs during further heat treatment which depends on the substrate. After annealing the crystalline films at 900°C

for 2 hours an increased crystallite size of 380 nm (α - Al_2O_3) and 220 nm (silicon) was found. The reasons for these differences were investigated by X-ray diffraction and infrared spectroscopy.

Table 1

Crystallite size of the barium titanate perovskite phase (determined from the width of the BaTiO_3 (111) reflection by the approximation method [12]).

substrate	temperature [$^{\circ}\text{C}$]	crystallite size [nm]
silicon	680	170
silicon	730	190
silicon	900	220
alumina	630	190
alumina	900	380

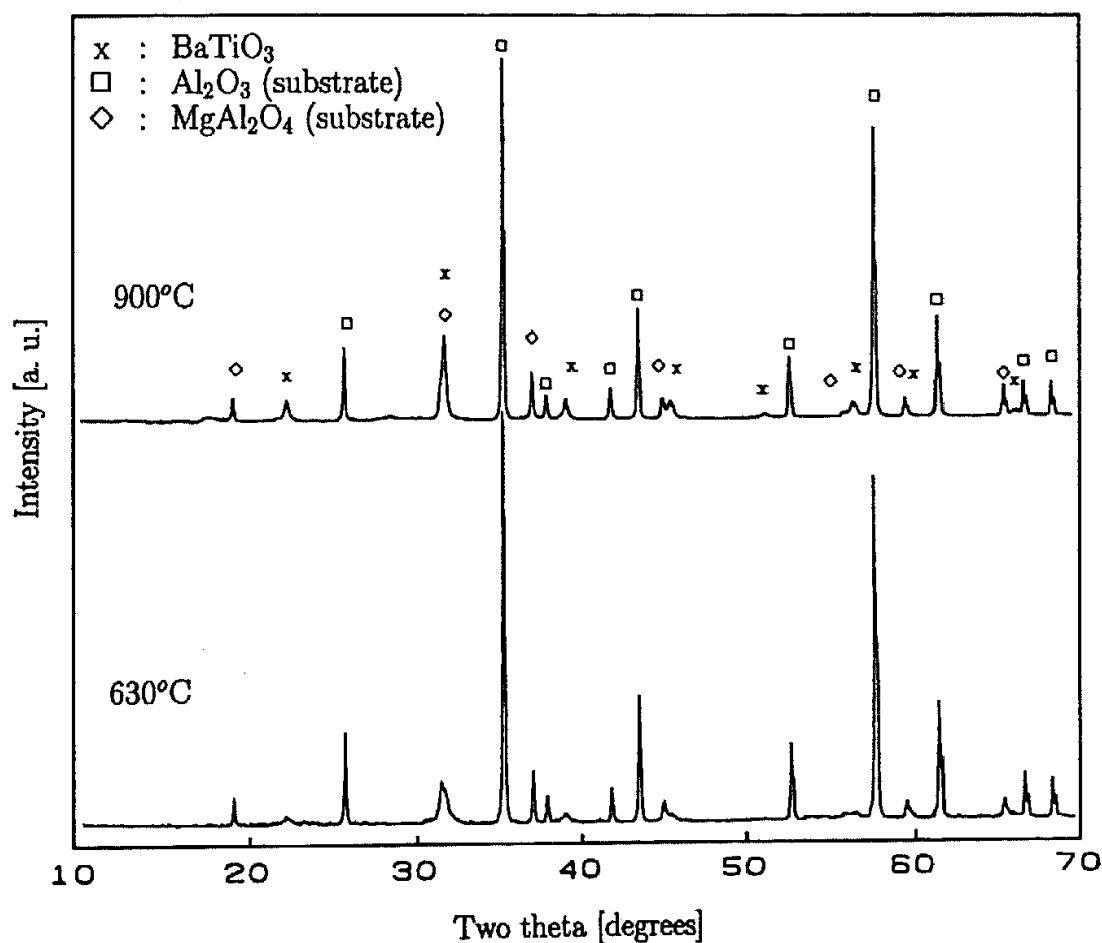


Figure 2. X-ray diffraction patterns of barium titanate films on MgO stabilized alumina as a function of firing temperature. The peak location for 630°C is the same as for 900°C.

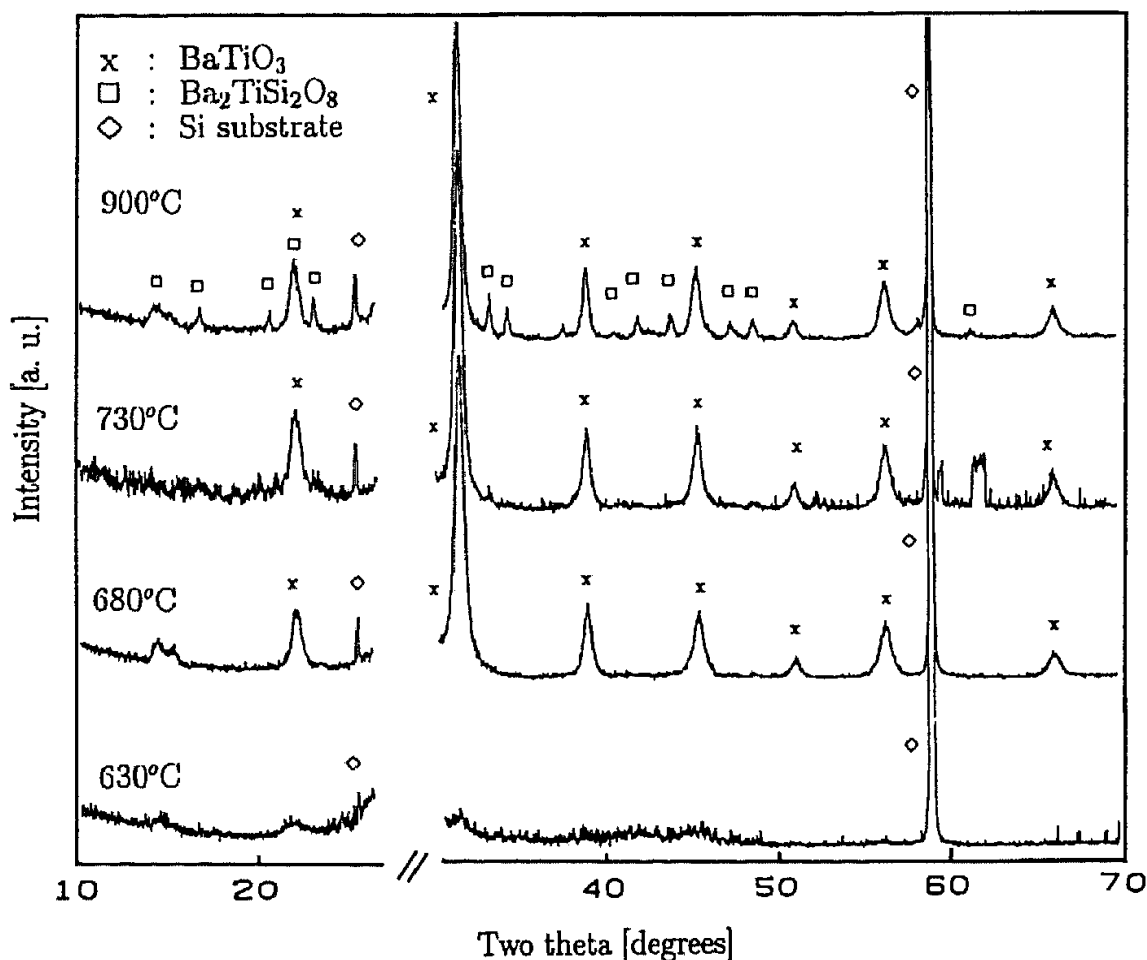


Figure 3. X-ray diffraction patterns of barium titanate films on silicon as a function of firing temperature ($2\theta = 27^\circ$ to 30° not measured because of the very intensive silicon (111) single crystal reflection).

Generally, the films are X-ray amorphous and crystallization takes place above 600°C . On alumina substrate (Rubalit 708, 96 % Al_2O_3) BaTiO_3 crystallizes at 630°C . The patterns of the film agree well with the ASTM values for tetragonal BaTiO_3 [13], but the line broadening effects prevent an absolute distinction between the tetragonal and the cubic crystal structure because of the very small deviation of the c/a ratio from unity. Spectra taken from films fired at higher temperatures differ only in line widths based on different crystallite sizes.

In contrast to Al_2O_3 as substrate the crystalline phases of films deposited onto silicon depend strongly on the calcination temperature. Up to 650°C the films are X-ray amorphous and the single-phase BaTiO_3 perovskite structure was detected at 680°C by X-ray diffraction. The higher crystallization temperature in comparison to alumina substrate is due to the bigger lattice mismatch between silicon and BaTiO_3 . After heat treatment at higher temperatures the films consist of the crystalline phase BaTiO_3 and $\text{Ba}_2\text{TiSi}_2\text{O}_8$

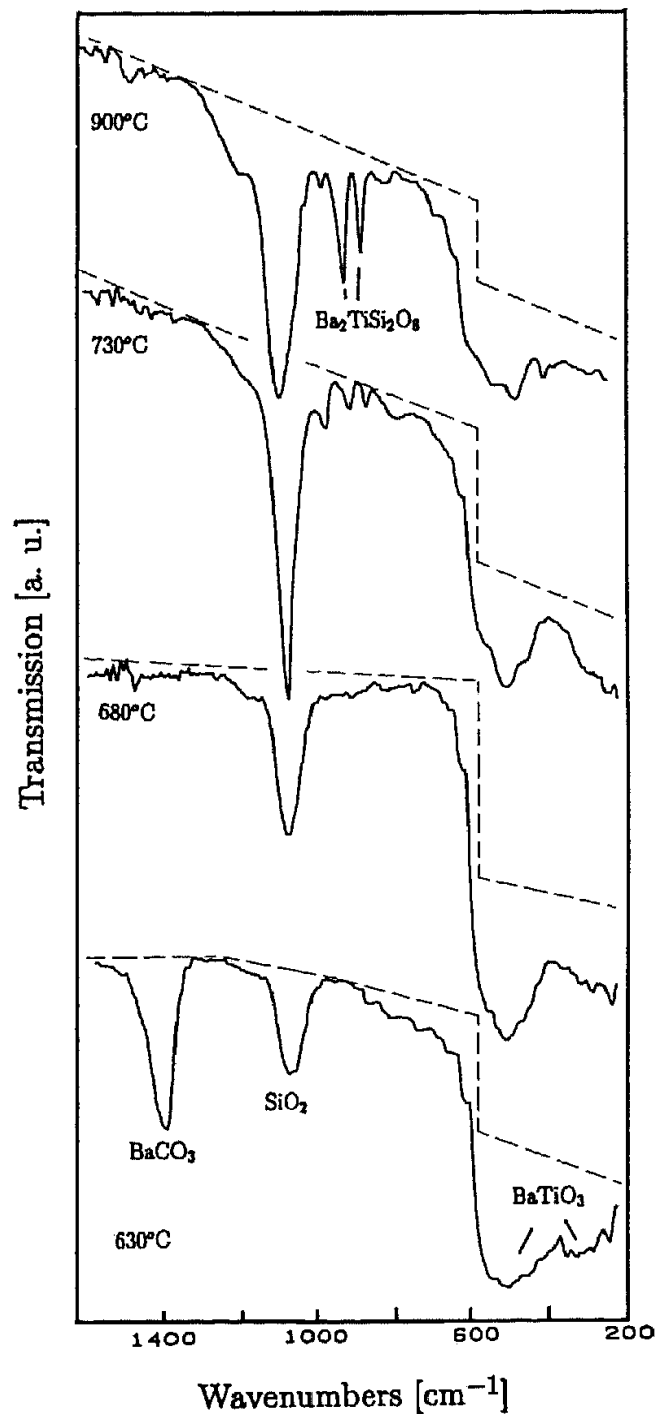


Figure 4. Infrared spectra of barium titanate films on silicon as a function of firing temperature (the dashed line represents the baseline and is an artefact from the spectrometer).

(fresnoite) [14]. The formation of fresnoite occurs between 730 and 900°C and is attributed to the reaction of BaTiO₃ or its precursors with the SiO₂ layer of the silicon surface. This is in agreement with the results reported in [15]. It was shown there that in the

system BaO/TiO₂/SiO₂ fresnoite is one thermodynamically stable crystalline compound. However, temperatures above 1300°C were needed for the formation of Ba₂TiSi₂O₈ from mixed oxides, which is much higher than found in this work ($T \leq 900^\circ\text{C}$). The reason for the low crystallization temperature is probably due to the small grain size of the reacting compounds which leads to an increased diffusivity and a lower crystallization temperature.

Infrared analysis gave some important additional informations about the phase transformations of the films on silicon substrates. Fig. 4 displays the infrared absorption bands for different temperatures. SiO₂ is found for all specimens at 1080 cm⁻¹ because the oxide layer on the substrate surface grows during thermal treatment in comparison to the unfired reference material. Absorption bands of silicon are eliminated by the reference because the silicon content is not affected by the heating procedure. Traces of BaCO₃, which are not found by X-ray diffraction, are recorded at 630°C. It is also detected at this temperature that the BaTiO₃ is already formed. The formation of barium titanate begins through the interaction of BaCO₃ and titanium-oxygen complexes [16]. At 680°C the barium carbonate is not present any more. By X-ray diffraction the BaTiO₃ phase is first detected at 680°C. In the same way the formation of the Ba₂TiSi₂O₈ phase is observed earlier with respect to temperatures of firing by infrared spectroscopy than by X-ray diffraction. Thus, the infrared spectroscopy could be used as a very sensitive tool for imaging the first step of the crystallization of the new phase.

4. CONCLUSIONS

The employed alkoxide-hydroxide route can produce single-phase BaTiO₃ films with perovskite structure. The crystallization behaviour and crystal phase development of the heat-treated amorphous gel films depends on the substrate material.

After crystallization further thermal treatment is necessary in order to attain crystallite growth, because high dielectric constants are associated with a minimum crystallite size. At higher temperatures it is important to attend to thin surface layers on the substrate, e. g. SiO₂ on silicon, which can lead to secondary phases in addition to the BaTiO₃ perovskite phase. In very thin films this reaction produces a considerable amount of impurities that impair the dielectric properties. Therefore the careful control of surface reactions during thermal processing is necessary to obtain BaTiO₃ films with optimum dielectric properties.

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