Kinetic of phase transformation of $SrBi_2Ta_2O_9$ deposited by metalorganic decomposition on platinum electrodes

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$SrBi_2Ta_2O_9$ thin films were prepared by metalorganic decomposition on $Pt/Ti/SiO_2/Si$ substrates and subsequently crystallized at temperatures ranging from 600 to 700 °C for 40 to 225 min. Data of the Aurivillius surface coverage taken from atomic force microscopy measurements were used to model the kinetics of isothermal phase transformation from the fluorite to the Aurivillius phase. A two-dimensional growth mechanism at a decreasing nucleation rate can be deduced. By evaluating the temperature dependence of the growth rates, an activation energy for phase transformation of 318 kJ/mol is determined. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1526926]

In the last decade, $SrBi_2Ta_2O_9$ (SBT) has been extensively studied for ferroelectric nonvolatile random access memory applications.[1,2] In comparison to other materials like $Pb(Zr,Ti)O_3$, SBT is distinguished by its capabilities for application in low-voltage devices and by its good fatigue performance.[3,4] The main disadvantage of SBT for use in ferroelectric random access memory devices is the required high processing temperature.[5,6] Especially for the integration of SBT into a stacked capacitor high-density memory architecture, a low thermal budget is necessary for processing. Therefore, the crystallization of SBT into the ferroelectric phase at the lowest possible temperature is needed to ensure further progress in technology development toward high-density memory devices.

During the past years, much effort has been put into reducing the temperature of SBT crystallization while keeping the electrical performance constant. Usually, the crystallization path of SBT occurs from the amorphous (as deposited) state over the metastable and nonferroelectric fluorite phase to the desired ferroelectric Aurivillius phase.[7] Therefore, SBT has to undergo two crystallographic phase formations until it reaches the final ferroelectric phase. While formation of the fluorite phase is completed at about 575 °C, the transformation into the more complex Aurivillius structure starts at temperatures of about 625 °C as a secondary phase and is completed at about 800 °C.[8] In this letter, we report the kinetics of nucleation and grain growth of the Aurivillius phase. With this, the processing conditions can be optimized to provide approaches for a low-temperature process. Simultaneously, an alternate and simple way to study the transformation kinetics of SBT will be presented.

The SBT thin films were deposited on $Pt/Ti/SiO_2/Si$ substrates by a metalorganic decomposition technique, which has been described in detail elsewhere.[9] A commercially available solution of octane based Bi, Sr, and Ta precursors was diluted using butylacetate to a concentration of 0.12 mol/l and deposited onto the substrate by spin coating. Removal of organic compounds was realized by a two-step hot plate treatment at 160 °C for 1 min and at 260 °C for 4 min. Subsequently, a rapid thermal annealing step was performed for 30 s at 650 °C in a pure oxygen ambient. For crystallization of the amorphous SBT films, an additional anneal in a diffusion furnace was performed. Anneals at 600 °C, 650 °C, and 700 °C for 40–225 min were used for the investigation of the nucleation and grain growth kinetics. The chosen film thicknesses were 40 nm and 90 nm. The exact stoichiometry of SBT film, determined by x-ray fluorescence was $Sr_{0.85}Bi_{2.2}Ta_2O_9$. To obtain topographic and morphological information, the films were investigated by atomic force microscopy (AFM) using a Nanoscope Dimension 3100 tool from Digital Instruments.

Figure 1 shows AFM surface images of 40 nm SBT films on Pt that were crystallized at 650 °C and 725 °C. The chosen processing temperatures are in the temperature regime of phase transformation from nonferroelectric fluorite to ferroelectric Aurivillius phase. Both images show a different microstructure and morphology. With these images, the path of crystallization to the Aurivillius phase can be illustrated. At 650 °C, the surface is mainly covered by the very fine grained and smooth fluorite phase. The size of fluorite grains is about 30 nm, and the root-mean-square value of the roughness was determined with 3.9 nm. Small, mostly circularly shaped Aurivillius nuclei protrude from the matrix and are homogeneously distributed over the investigated scan area. The film appears to be uniform all over the surface.

At an increased annealing temperature, the crystallization into Aurivillius phase is advanced. The share of Aurivillius phase in the film has increased, which is due to ongoing nucleation and grain growth processes within the SBT film. In the early stage of crystallization, most of the Aurivillius grains are separated by a clearly defined grain boundary. At an advanced stage, a possible merging of Aurivillius grains can be observed resulting in clearly less grain boundaries. Figure 1(b) shows all four stages during the crystallization process: (1) the original fluorite phase as a metastable phase as well as (2) the nucleation, (3) the grain growth, and

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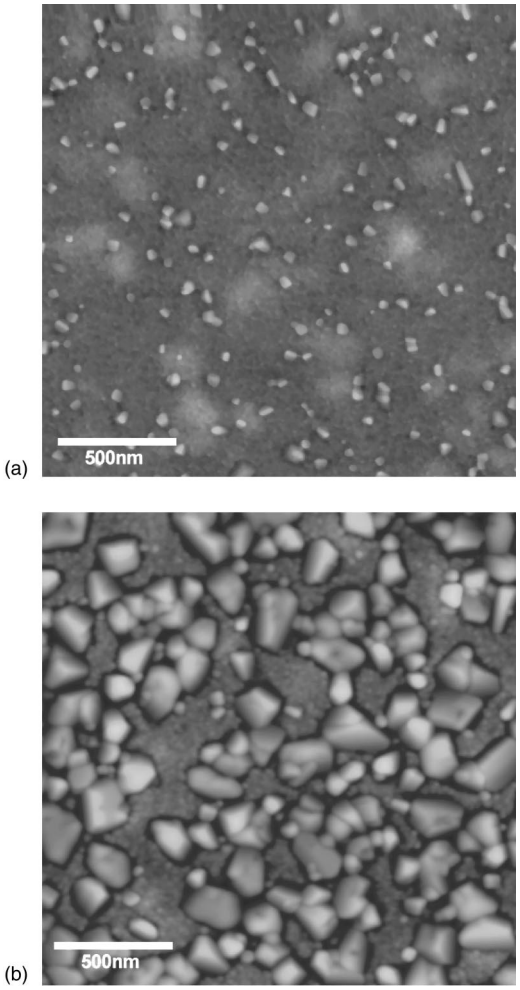

FIG. 1. AFM images of 40 nm thick SBT films crystallized at 650 °C (a) and 725 °C (b) for 45 min. The z range of the $2\times2\ \mu m^2$ images is 100 nm. The ferroelectric Aurivillius phase can be seen as granular protrusions from the fine grained matrix of fluorite phase.

(4) the coalescence/merging of Aurivillius grains. Two main processes defining the phase transformation can be separated from this: The nucleation and the growth of Aurivillius grains. A further increase in the thermal budget (higher annealing temperature or longer time) results in an SBT film that completely consists of Aurivillius grains.

In order to assess the nucleation process of small Aurivillius grains, only films crystallized near the conditions of the

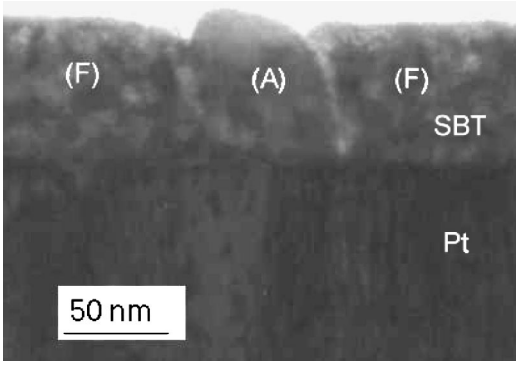

FIG. 2. Transmission electron microscopy cross-sectional image of a 68 nm SBT film crystallized at 650 °C for 45 min. An Aurivillius nucleus (A) with a diameter in the order of the film thickness can be seen within a fine grained fluorite matrix (F).

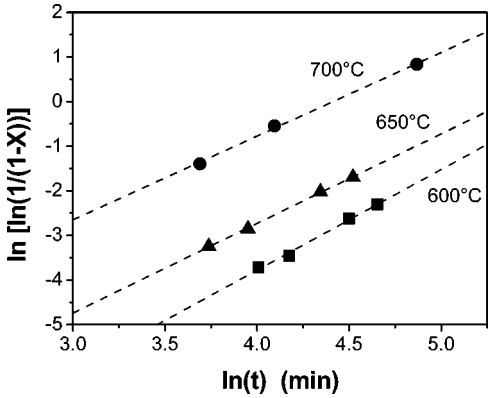

FIG. 3. Avrami plots of isothermal phase transformations from fluorite to Aurivillius phase of SBT for three different temperatures of the crystallization anneal. The anneal time for all samples was between 40 min and 225 min. From the slopes, Avrami coefficients close to $n=2$ can be determined for all investigated annealing temperatures.

phase transformation are investigated. The kinetics of transformation from fluorite to Aurivillius phase can be described by the Johnson–Mehl–Avrami theory.[10,11] Here, the transformed volume fraction $V(t)$ is expressed as a function of time t. Since the diameter of the small Aurivillius nuclei is in the range of the SBT film thickness d (see Fig. 2), the description of a usually three-dimensional crystallization process can be simplified into a two-dimensional one. Thus, for the description of the nucleation and growth, only the surface coverage $X(t)=V(t)/d$ of Aurivillius grains is of interest. Then, the transformation process can be described by a modified Johnson–Mehl–Avrami equation

$$X(t)=1-\exp(-Kt^n), \tag{1}$$

where $K(T)$ is a temperature dependent rate constant and n is the Avrami coefficient. The coverage data were collected from AFM measurements of SBT samples annealed at different temperature–time combinations. The Avrami coefficients n are extracted from a series of isothermal Avrami plots of $\ln[\ln(1/(1-X))]$ versus $\ln(t)$, where n is the slope and the y intercept is $\ln(K)$. In Fig. 3, the measured data agree very well with nucleation and growth theory of Avrami. The extracted values for Avrami coefficients n and $\ln(K)$ are summarized in Table I. It can be seen that for all investigated annealing temperatures, the Avrami coefficients are close to a value of $n=2$, which is reasonable as they indicate a two-dimensional grain growth from small dimensions at a decreasing nucleation rate.[12] Decreased Avrami coefficients n can be observed at increased annealing temperatures T. This can possibly be explained by a reduction of nucleation rate at increased temperature due to an increased surface coverage of the Aurivillius phase.

TABLE I. Kinetic parameters of isothermal nucleation and grain growth of SBT from Avrami plots.

Temperature T (°C)	$\ln K$	Avrami coefficient n
600	-12.79 ± 0.55	2.25 ± 0.13
650	-10.76 ± 0.30	2.01 ± 0.04
700	-8.27 ± 0.32	1.88 ± 0.08

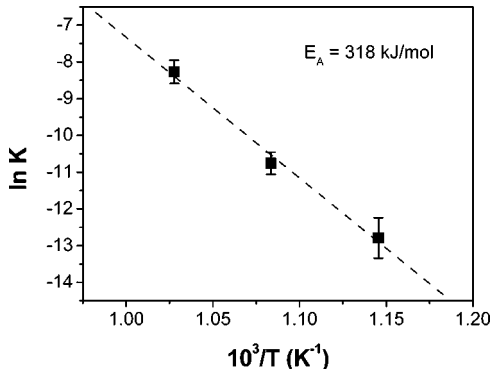

FIG. 4. Arrhenius plot of rate constants from Avrami plots. An activation energy for the phase transformation of $E_A = 318$ kJ/mol can be deduced.

The rate constants K determined from the Avrami plots were used to determine the activation energy E_A for the phase transformation, using the Arrhenius expression

$$K = K_0 \cdot \exp\left(\frac{E_A}{k_B T}\right), \tag{2}$$

where k_B is Boltzmann's constant. From the Arrhenius plot of $\ln(K)$ versus reciprocal temperature $1/T$, as shown in Fig. 4, an activation energy of $E_A = 318$ kJ/mol was found. These results provide a quantitative prediction of the phase transformation for any given temperature–time combination. The extracted activation energy for SBT fits very well to the work of *Sung*[13] which determined a value of 375 kJ/mol by using the differential thermal analysis method.

To summarize, the grain structure of SBT crystallized in the regime near the phase transformation from fluorite to Aurivillius phase was characterized by the AFM technique. A large difference in microstructure of the phases was observed. From these AFM images, the kinetics of nucleation and grain growth could be determined by the application of the Avrami theory. Crystallization of Aurivillius grains occurs via a two-dimensional growth process at a decreasing nucleation rate. The activation energy for the phase transformation can be estimated to be 318 kJ/mol.

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