Numerical investigations of laser-induced crystallization and stress development in phase changes of electroceramic materials

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ABSTRACT

Barium-Strontium-Titanate, BST, in the stoichiometry $Ba_{0.7}Sr_{0.3}TiO_3$ to $Ba_{0.5}Sr_{0.5}TiO_3$ is been considered as a promising candidate to enter into the DRAM manufacturing technology. The incompatibility between the temperatures required to crystallize the ferro/para-electric layer into the required Perovskite phase and the thermal budget of underlying active circuitry rules out the application of conventional, quasi-stationary heat treatment of these new materials when integrating into the circuit fabrication process. Therefore, the research focuses on heating amorphous ceramic thin films by laser radiation with pulse durations in the ns regime to induce changes in their structural and electronic properties in the heated region only. To establish initial operating parameters for the laser-induced crystallization and to study the amorphous to crystalline phase transformation including stress formation a simulation program is developed. The model includes heat transfer, crystallization and thermal respective phase transformation induced stress analysis.

Keywords: Laser crystallization/annealing, thin films, $(Ba,Sr)TiO_3$, stress analysis.

1 INTRODUCTION

Electroceramic materials feature a great number of interesting properties, like ferro-electricity, electro-/magneto-optical, piezo- or pyro-electrical effects, which all can be used in novel devices with unique functionality, hard to be achieved by using conventional materials and processing. Gbit memory modules, high sensitive sensors, and nano-actuators are examples of devices to come. The incompatibility between the temperatures required to crystallize the ferro/para-electric layer into the required Perovskite phase and the thermal budget of underlying active circuitry initiate the research to focus on heating amorphous ceramic thin films by laser radiation with pulse durations in the ns regime to induce changes in their structural and electronic properties in the heated region only. The possibility of a phase transformation from an amorphous to a x-ray cristalline phase by pulsed laser irradiation has already been reported for $(Ba,Sr)TiO_3$ [1-4]. The further process development of laser crystallization of thin $(Ba,Sr)TiO_{3\ films}$ will be performed with the help of a mathematical approach. The present paper introduces a three dimensional axially symmetric model to describe the thermalization of optical energy, heating of a multilayer structure, crystallization, and stress development due to inhomogeneous temperature distribution, mismatch of coefficients of thermal expansion between different layers, and the material contraction during amorphous to crystalline phase transformation. The governing equations are integrated by the Finite Element method using two-dimensional second order elements of the Serendipity class with eight nodes per element [5].

2 PHYSICS OF CRYSTALLIZATION

2.1 Processes

A three dimensional axially symmetric analysis is presented which models a circular source laser beam striking the surface of a transparent material of thickness D (Fig.1). Part of the incident radiation is reflected, while the remaining one penetrates into the material to become continuously absorbed in accordance with the Lambert law. The absorbed optical energy is converted to thermal energy raising the temperature. The increasing temperature initiates the transformation from an amorphous to a crystalline phase whereby the fraction of transformed phase in the following

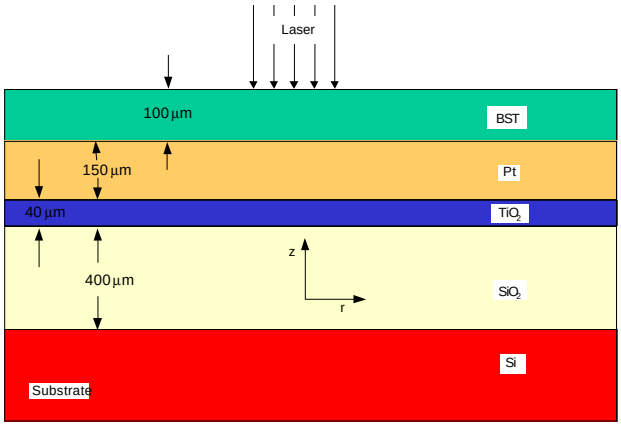

Fig. 1: Model Geometry.

named X at time t is computed using the Jonson-Mehl-Avrami (JMA) kinetic equation in the modified version for non-isothermal temperature cycle. The non-homogenous temperature distribution and the material contraction due to the phase transformation gives rise to thermal and phase transformation stresses in the film which may initiate crack formation. For the computation of stress distribution within the film a thermoelastic model is applied.

2.2 Mathematical Formulation

The appropriate governing equations are as follows:

- heat equation

$$\frac{\partial(\rho c_p T)}{\partial t} = \nabla(\lambda \nabla T) + q_L$$

$$with: q_L = \frac{A \cdot I_L(r,t)}{\delta_{opt}} \cdot \exp\left(-\frac{z}{\delta_{opt}}\right) \qquad (1)$$

- Johnson-Mehl-Avrami equation

$$X(t) = 1 - \exp\left[-(kt)^n\right] \qquad (2)$$

$$with: \; k = v_o \cdot \exp(-E_a / RT)$$

- thermo-elastic stress/strain equations

$$div\underline{\underline{\sigma}} = \frac{\partial \sigma_{ij}}{\partial x_j} = 0 \qquad (3)$$

$$\sigma_{ij} = \frac{E}{1+\nu}\varepsilon_{ij} + \frac{E\nu}{(1+\nu)(1-2\nu)}\varepsilon_{kk}\delta_{ij} - \frac{\alpha \cdot E \cdot \Delta T}{(1-2\nu)}\delta_{ij} - \frac{\alpha_c \cdot E \cdot X}{(1-2\nu)}\delta_{ij}$$

$$with \varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u^i}{\partial x_j} + \frac{\partial u^j}{\partial x_i}\right)$$

Equations (1) to (3) are subjected to the following initial and boundary conditions:

$$T(r,z,t) = T_u \;\; (initial\,temperature\,distribution)$$

$$X(r,z,t) = 0 \;\; (initial\,amorphous\,material)$$

$$\lambda \frac{\partial T}{\partial z}(r, z=0) = 0 \;\; (adiabatic\,boundary)$$

$$u_r(r=0,z,t) = 0 \;\; (no\,radial\,displacement\,due\,to\,symmetry\,at\,the\,centerline)$$

$$u_z(r=0,z=0,t) = 0 \;\; (elimination\,of\,translational\,degree\,of\,freedom)$$

3 RESULTS AND DISCUSSION

Fig. 2 shows the laser pulse shape as used in the heat transfer analysis. The discontinuity in the isolines of temperature field (Fig.4) is caused by the discontinuous change of material properties within the layered system. The crystalline phase penetrates up to 20 nm into the film (Fig. 5) which equals approximately the optical penetration depth. The transformation from an amorphous to a crystalline phase is finished in the cooling phase where the temperature undergoes 1260 °C. The stress distribution shows during the heating phase in the BST film exclusive compressive stress due to hindered thermal expansion (Fig.6). After cooling down to total temperature homogenization at the initial temperature T_u a tensile stress distribution remains due the material contraction after the amorphous to a crystalline phase transformation (Fig.7) which may initiate crack formation.

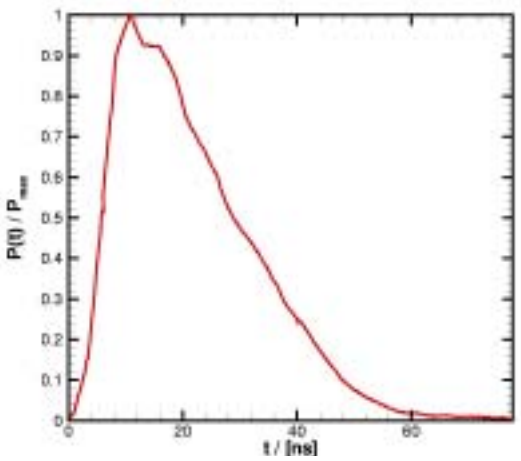

Fig. 2: Laser pulse shape.

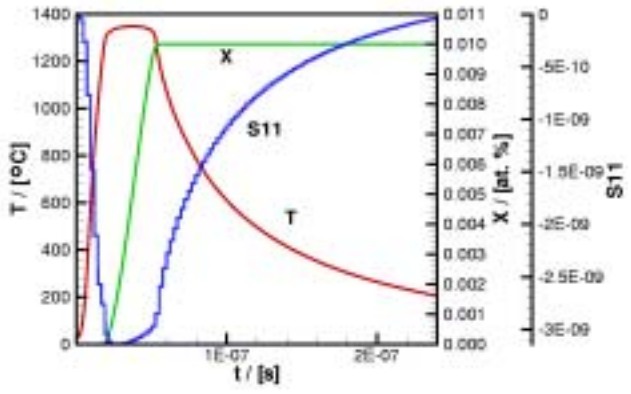

Fig.3 Temperature T/ [°C], fraction of crystalline phase X / [V%] and radial stress σ_{rr} (=S11) / [N/nm^2] at center point (r=z=0) as a function of time, D=200nm, I=80mJ/cm, A=0.87,δ_{opt} =19nm.

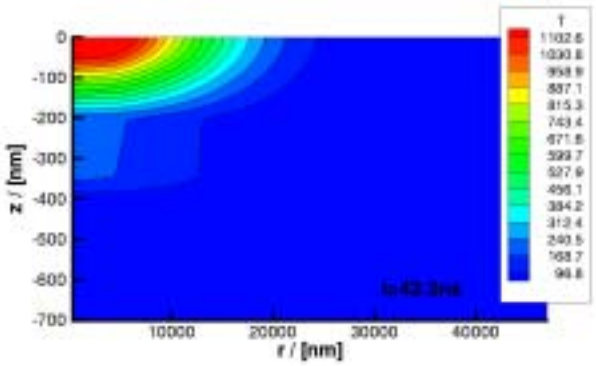

Fig.4: Temperature distribution T/[°C] at time t=43.2ns (parameters see Fig.3).

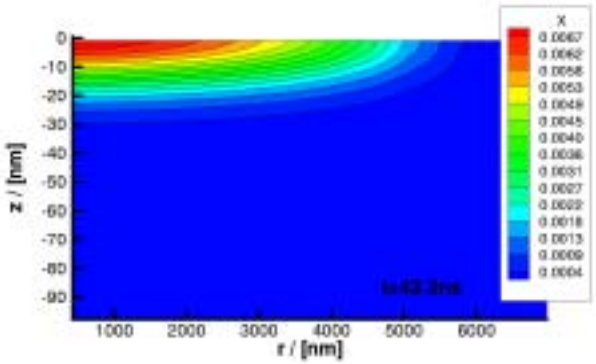

Fig.5: Fraction of crystalline phase X / [V%] at time t=43.2ns (parameters see Fig.3).

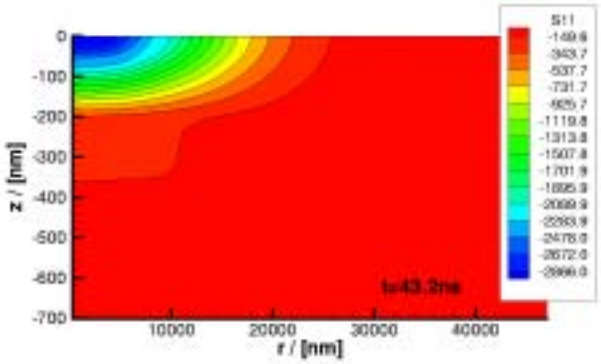

Fig.6: Radial stress component σ_{rr} (=S11) / [N/nm^2] at time t=43.2ns (parameters see Fig.3).

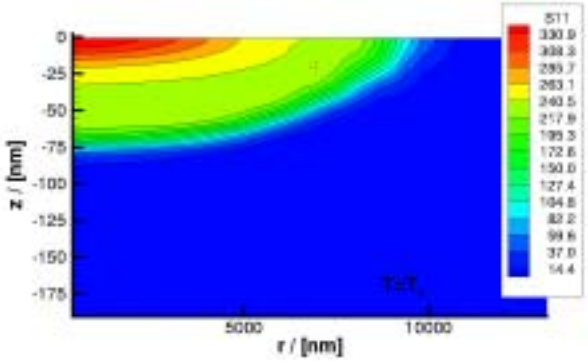

Fig.7: Residual radial stress component σ_{rr} / [N/nm^2] after temperature homogenization T=T_u (parameters see Fig.3).

The laser crystallization is an incremental process whereby the desired fraction of crystallized phase is be attained by application of consecutive laser pulses. The simulation shows an approximately linear increase in the fraction of crystallized phase per laser pulse (Fig. 9) whereby the residual tensile stress increases continuously with increa-

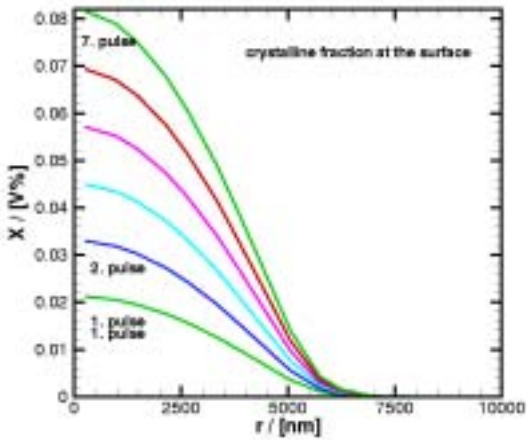

Fig. 9: Crystalline phase X(r,z=0) / [V%] at the surface for seven consecutive laser pulses whereby the temperature is cooled down homogenous to T=T_u after each pulse (parameters see Fig.3).

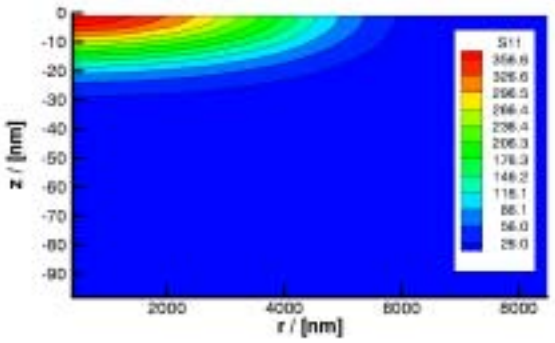

Fig.10: Residual radial stress component σ_{rr} (=S11) / [N/nm^2] after 3 laser pulses and temperature homogenization (parameters see Fig.3).

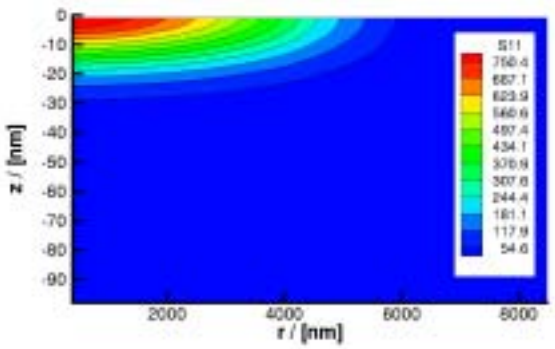

Fig.10: Residual radial stress component σ_{rr} (=S11) / [N/nm^2] after 6 laser pulses and temperature homogenization (parameters see Fig.3).

sing fraction (Fig. 10,11). Therefore, it may exist a critical limit for the fraction of crystallized phase above which the resulting tensile stresses may initiate crack formation.

4 SUMMARY

A three dimensional axially symmetric model is presented which describes the thermalization of optical energy, heating of a multilayer structure, crystallization, and stress development due to inhomogeneous temperature distribution, mismatch of coefficients of thermal expansion between different layers, and the material contraction during amorphous to crystalline phase transformation. The simulation results show that the crystallization has to be performed by application of consecutive laser pulses generating the desired fraction of crystallized phase. The temperature within the layers beneath the $(Ba,Sr)TiO_3$ film doesn't exceed the temperature limit of 450 ^oC during laser treatment. With increasing fraction of crystallized phase the residual tensile stresses within the film increase.

5 LIST OF SYMBOLS

λ: heat conductivity
ρ: density
c_p: heat capacity
A: absorbance
I(r,t): laser intensity distribution
δ_{opt}: optical pentration depth
E: Young modulus
ν: Poisson ratio
u: component of displacement vector
ε: strain tensor
σ: stress tensor
X. crystalline phase
E_a: Arrhenius activation energy
ν_o: vibration frequency
k: reaction rate
n: Avrami exponent

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