Ion-plasma deposition of multicomponent films with a given law of composition distribution by thickness

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A method is proposed for ion-plasma deposition of thin multicomponent films with the ability to control the component composition in thickness (graded film) with a change in the pressure of the working gas according to a given law. Using the $Ba_xSr_{1-x}TiO_3$ (BSTO)perovskite-type structure as an example, the calculated (Monte Carlo simulation) and experimental dependences of the component composition of films and their deposition rate on the pressure of the working gas were obtained. As an example, the possibility of deposition of BSTO films with a linear distribution of composition by their thickness.

Keywords: ion-plasma deposition, thin multicomponent films, composition control.

The properties of multicomponent ferroelectric materials (films and ceramic materials) depend strongly on the elemental ratio of divalent Ba and Sr ions occupying cuboctahedral sites in the perovskite lattice. Varying the ratio of components, one may alter the structure and electric characteristics of materials. This feature is much needed in various practical applications [1–9]. A change of targets is currently required to fabricate a film with the composition varying over its thickness (graded film) by ion-plasma deposition. This change induces „steps" in film composition and unwanted defects of interphase boundaries. In the present study, we propose a method of ion-plasma deposition onto a substrate that provides an opportunity to fabricate multicomponent films with controlled continuous variation of composition over their thickness using a single target. The method relies on variation of the directional properties of fluxes of sputtered target atoms as a result of their thermalization and transition to a diffusion motion mode, which are induced by changes in the working gas pressure in the process of film growth [10,11].

The variation of component composition of ferroelectric films of $Ba_xSr_{1-x}TiO_3$ perovskites synthesized under different working gas pressures in a sputtering system with a $Ba_{0.3}Sr_{0.7}TiO_3$ target (Leybold Z400 setup) was examined experimentally. Al_2O_3 (r-cut) substrates were used for deposition at temperature $T_s = 780°C$ and target−substrate distance $d_{t-s} = 2.5$ cm. The working gas (O_2) pressure in the deposition chamber was measured at several points within the $P = 2-60$ Pa interval. Following deposition, the films were cooled to room temperature in the atmosphere of pure oxygen at a rate of $2-3°C$/min. The film thickness fell within the range of $100-300$ nm. Composition $x(P)$ of deposited films varied within the range of $x = 0.15-0.32$

(Fig. 1) as the working gas pressure increased from 2 to 60 Pa. This agrees with the results of medium-energy ion scattering (MEIS) experiments presented in the inset of Fig. 1.

Data on the component composition of $Ba_xSr_{1-x}TiO_3$ were obtained via modeling of MEIS spectra of backscattering of He^+ ions with an energy of 227 keV by varying the iteration procedure parameters [12].

Statistical Monte Carlo modeling [10,13] of the processes of ion-plasma target sputtering and transport of sputtered particles within the target−substrate space was performed for the process parameters corresponding to the experimental sputtering setup. The results of simulation (dashed curve in Fig. 1) agree within 10% with the experimental data.

The measurement of experimental dependence $x(P)$ characterizing the composition of the solid solution (Fig. 1)
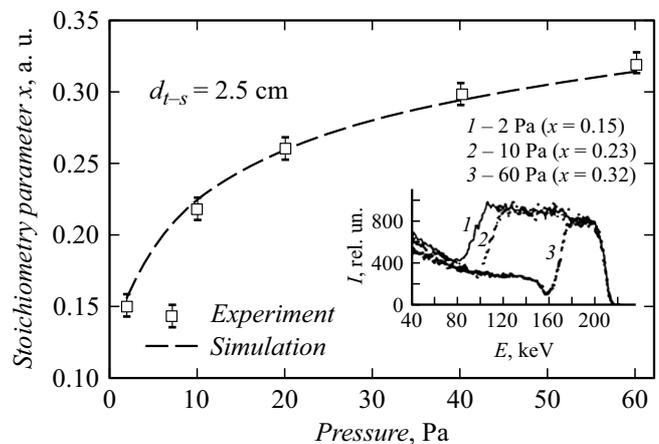

Figure 1. Experimental and calculated dependences of solid-solution composition parameter x on the working gas pressure for $Ba_xSr_{1-x}TiO_3$ films.
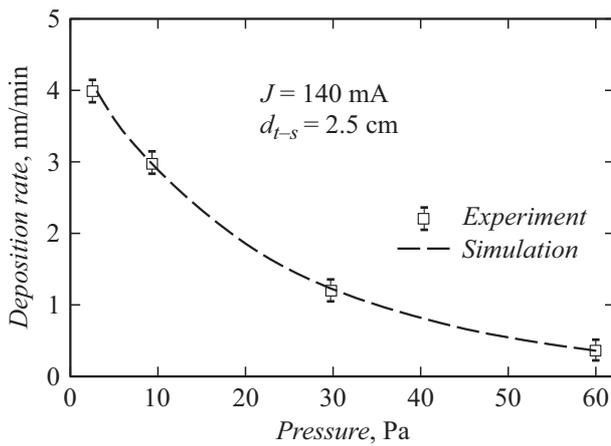
Figure 2. Experimental dependence of the deposition rate of $Ba_xSr_{1-x}TiO_3$ films on the working gas pressure.

allows one to determine the time dependence of pressure $P(t)$ corresponding to given distribution $x(d)$ of parameter x over the thickness of a growing film in the process of deposition. It should be taken into account that a change in pressure $P(t)$ induces significant variations both of $x(d)$ and film deposition rate $V_{dep}(P)$. Therefore, the dependence of the deposition rate of $Ba_xSr_{1-x}TiO_3$ films on working gas pressure P at discharge current $J = 140\,mA$ was also examined experimentally (Fig. 2).

The approximations of experimental dependences $x(P)$ and $V_{dep}(P)$ in Figs. 1 and 2 take the form of $x(P) = 0.05\ln P + 0.12$ and $V_{dep}(P) = 4.553\exp(-0.045P)$ within an error of 10%.

Dependence $P(t)$ in the process of film deposition is the solution of equation $x[P(t)] = x[P(V_{dep})]$ for function

of distribution (specified in a general form) of the stoichiometry parameter over the growing film thickness $x(d)$, which is an $x[P(t)]$ functional. This approach allows one to synthesize films with a given distribution $x(d)$ of solid-solution composition parameter x over the growing film thickness.

Lets us consider the example of a linear distribution of this kind for $Ba_xSr_{1-x}TiO_3$ with the following boundary conditions: $x(d = 0) = 0.15$ and $x(d = h) = 0.32$, where h is a finite film thickness. The linear $x(d)$ distribution for the given range of parameter variation in the process of film deposition ($d \in [0-300]\,nm$ and $P \in [2-60]\,Pa$) takes the following form: $x(d) = 0.00056d + 0.15$ (Fig. 3, a). It is evident that variation $P(t)$ of the working gas pressure should be characterized in this case by function $P(t) = a\exp(bt)$ (Fig. 3, b), which is inverse to experimental dependence $x[P(t)] = c\ln P + d$ (Fig. 1). It is necessary to take into account the experimental dependence of the rate with experimental dependence $V_{dep}(P) = e\exp(-fP)$ (Fig. 2), where a, b, c, d, e, f are approximation coefficients calculated based on experimental data. In the present example, $a = 2$, $b = 1.31$, $c = 0.05$, $d = 0.12$, $e = 4.553$, and $f = -0.045$. Thus, if working gas pressure P varies from 2 to $60\,Pa$ in the process of deposition of a film with thickness h in accordance with the $P(t) = 2.0\exp(1.31t)$ law, a linear distribution of parameter $x(d) = 0.00056d + 0.15$ of the solid-solution composition over the thickness of a growing film is obtained.

Hence, the determination of experimental dependences $x(P)$ and $V_{dep}(P)$ is the basis for setting the technological regime of ion-plasma deposition of films with a predefined distribution of the component composition over their thickness.
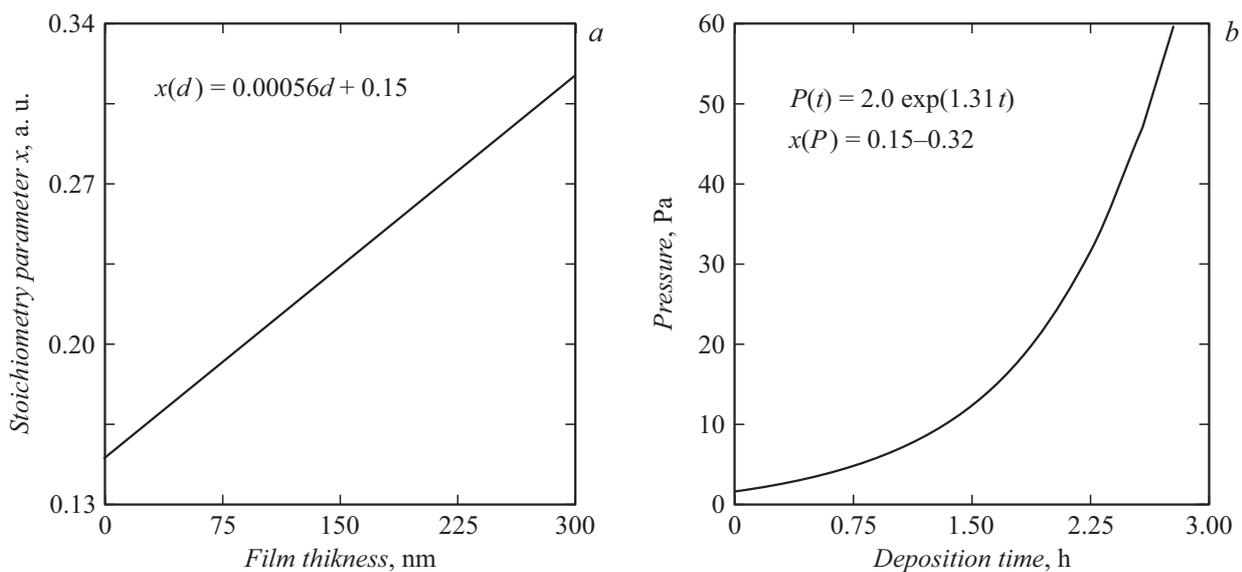

Figure 3. Given distribution $x(d)$ of solid-solution composition parameter x over thickness d of a growing film (a) and calculated variation $P(t)$ of the working gas pressure (b) in the process of deposition of $Ba_xSr_{1-x}TiO_3$ films.

Conflict of interest

The authors declare that they have no conflict of interest.

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