EPITAXIAL STABILIZATION IN MOCVD OF OXIDE THIN FILMS

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In this paper which is a survey of recent authors results it is shown that many oxides which are thermodynamically unstable in bulk state can be obtained as thin epitaxial films using thermal MOCVD. This new synthetic approach, named *epitaxial stabilization* can be an effective tool in materials chemistry able to enlarge the spectrum of novel epitaxial functional materials.

In the thin film growth the disagreement of the phase composition with the equilibrium phase diagrams is not a rare phenomenon being of kinetic or thermodynamic origin: the formation of some phases occurs often at the thermodynamic conditions which are far beyond the stability range of corresponding phase in the bulk form. We concluded that in case of thermal MOCVD of oxides these phenomena are definitely of thermodynamic origin and follow to the Dankov – Van der Merwe principle [1]. The stabilization of in bulk-unstable phase occurs due to structural coherency to the substrate or to the surrounding film matrix. The Gibbs' energy of a nucleus formation at the substrate is a sum of three terms –volume, surface and elastic ones:

$$\Delta G_f = \Delta g^{vol} V + \sigma S + \Delta G^{stress} .$$

The importance of positive surface term becomes predominant when the nucleus volume is small. As the surface energy of the coherent interface is much lower then that of incoherent one, the destabilizing action of surface term is much less in case of film/substrate structural coherency (epitaxy) and it can lead to the more stable state of epitaxial phase in thin film with respect to incoherent one which is stable in bulks.

The epitaxial growth of stabilized phase is limited in thickness: when the films exceeds some critical thickness "normal" phases predicted by equilibrium diagram of the system start to grow due to 1) predominance of volume term $\Delta g^{vol} V$ and 2) increased destabilizing role of elastic epitaxial stress expressed by the positive term ΔG^{stress}. The equation describing the critical thickness of epitaxially stabilized phase was derived for the case of two polymorphous phases , one of which is coherent and another one is incoherent to the substrate

$$h_c = \frac{\left(\sigma_{ic}'' - \sigma_c'\right)}{\left[\left(\Delta g'_V - \Delta g''_V\right) + \frac{\mu}{1-\nu}\varepsilon^2\right]}$$

where μ is a shear modulus, ν is a Poisson ratio for the coherent phase, ε is the lattice mismatch determined as $\varepsilon = \Delta a/a_s = (a_f - a_s)/a_s$ with the lattice spacing a_s and a_f for the substrate and the coherent film respectively, index ' is referred to the thermodynamic functions of nucleus of the epitaxial phase, the index " refers to the thermodynamic functions of nucleus of the incoherent phase.

As it can be seen from this formula and fig.1 the critical thickness of epitaxially stabilized phase decreases strongly with the increase of lattice mismatch at the

film/substrate interface as well as with the increase of free energy difference of unstable and equilibrium phases.
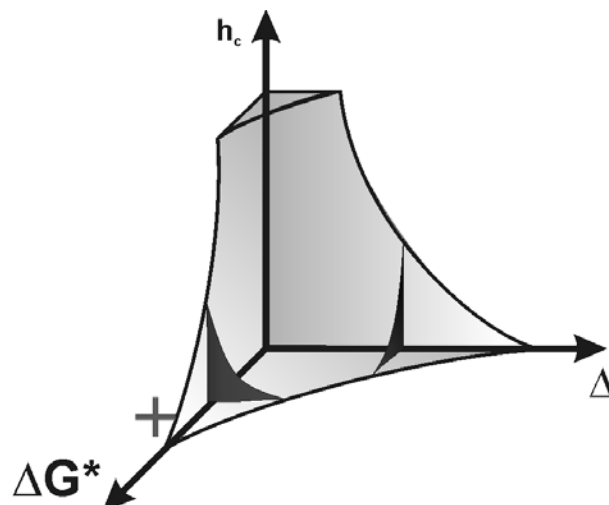

Fig.1 The effect of the free energy of the polymorphous transformation and the lattice mismatch on the critical thickness of epitaxially stabilized phase.

These dependences were confirmed in authors's practice of MOCVD of epitaxial films of ternary rare earth compounds $REBO_3$ (B=Mn, Fe, Ni, Co, In) on single crystalline substrates. The deposition was performed in the stagnation flow reactors using thd-chelates of corresponding metals as precursors, the later were delivered from the evaporators of flash type. The deposition temperature was in the range 650-900°C, oxygen pressure 3-10 mbars, deposition rate $\approx$ 3 nm/min. The films were characterized by XRD, SEM, EDX and HREM techniques as well as by conductivity measurements (for $RENiO_3$ and $RECoO_3$).

It was shown that the perovskites $RENiO_3$ (RE=Pr, Nd, Sm, Eu and Gd) and $RECoO_3$ (RE= Tm,Lu) which are unstable as bulk phases at the deposition conditions, can be obtained as epitaxial films on the well matched substrates of perovskite structure. In case of manganates $REMnO_3$ which form perovskite or hexagonal phases depending on the type of RE, the morphotropic series of perovskites, typical for larger RE was continued for smaller Ho-Lu members being deposited on perovskite substrates while these compounds are known as hexagonal phases in bulk state at the deposition conditions. Oppositely, the hexagonal phases, typical for smaller RE, were obtained also for larger Dy-Eu members on (111)YSZ substrate, while in bulk or on noncoherent substrate they are perovskites at deposition conditions [2]. Analogously , the $REInO_3$ were obtained as epitaxial perovskites on isomorphous substrate for Sm-Er members, while they are hexagonal in bulk state. Using this approach the hexagonal $REFeO_3$, unknown up to date, were for the first time obtained as epitaxial films on (111)YSZ.

The potential of epitaxial stabilization approach for new electronic materials was also demonstrated in preparing the heterostructures with in-plane alternating $NdNiO_3$ and $(La,Ca)MnO_3$ epitaxial components.

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