METALORGANIC AEROSOL DEPOSITION TECHNIQUE

TEHNOLOGIA DEPUNERII DIN AEROSOLII COMPUŞILOR METALORGANICI

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Thin-film oxide technologies such as radio frequency sputtering, pulsed laser deposition, oxides molecular beam epitaxy, plasma-enhanced chemical vapor deposition, metalorganic chemical vapor deposition, pulsed laser deposition, sol-gel coating, and spray pyrolysis allow material scientists to get high conducting (including transparent), semiconducting, insulating, ferroelectric, ferromagnetic, multiferroic films. Cost-effective chemical vapor deposition-based technologies can be quite competitive with vacuum film production methods, providing high crystalline quality and uniformity over a large area. One of the bottlenecks of metalorganic chemical vapor deposition is the limited range of organometallic compounds, namely, only volatile compounds can be used. This limitation can be overcome by liquid-assisted metalorganic chemical vapor deposition using an injection of the metalorganic precursor solution into the growth zone. Another disadvantage of the vacuum-free technology is the impossibility of manipulating film growth with high accuracy of composition and thickness. We continuously develop Metalorganic Aerosol Deposition (MAD) for to solve problems focused on design of artificial materials based on oxide films [1-4].

MAD is a cost-effective chemical vacuum-free technology previously engineered for the preparation of high-quality oxide thin films and further developed for the deposition of ultrathin films and superlattices. The MAD technology development stages are presented in Table 1. Figure 1 (a) shows a schematic representation of the 3rd generation MAD system. The MAD 3rd system is mainly focused on oxide films preparation, including the use of transition metals with stable oxidation states. The growth chamber is equipped with a substrate heater, pyrometer for substrate temperature monitoring, pneumatic nozzle with up to 4 liquid channels, laser – photodiode for aerosol flow control, and ellipsometry film growth control tool. Aerosols of organic solutions, containing metal β- diketonates (e.g., La-, Sr-, Mn-acetylacetonates), are sprayed onto a heated substrate. A film grows on the substrate as a result of a heterogeneous pyrolysis reaction of the metalorganic component. The heater ensures temperatures of 500-1000°C for epitaxial film growth of simple and complex oxides having thicknesses in the range of

1-200 nm. Films of complex oxides and films of simple oxides doped with an impurity can be prepared from a single solution containing all the necessary precursors. The correct ratio of cations in the film is the result of an accurate selection of the precursors ratio for the solution. The oxygen stoichiometry in the compounds is achieved due to the high partial pressure of O_2 in the chamber. Numerous channels make it possible to grow superlattices by alternating portions of the corresponding precursor solutions.

Table

Laboratory-built generations of MAD technique

Generation	**Deposition conditions**	**Controls and monitoring**	**Materials**
1	atmospheric pressure, single source	Substrate temperature pyrometer control, micropipette dosing	Single films, composites
2	atmospheric pressure, multisource, automation	Substrate temperature pyrometer control, laser-PD aerosol flow control, peristaltic pump dosing	Single films, multilayered structures, superlattices
3	atmospheric pressure, multisource, automation	Substrate temperature pyrometer control, ellipsometry growth control, syringe pump dosing	Single films, multilayered structures, superlattices, interface engineering
4	controllable atmosphere (Ar+O2), multisource, automation	Substrate temperature pyrometer control, ellipsometry growth control, syringe pump dosing	Single films, multilayered structures, superlattices, interface engineering, films with controllable transition metal oxidation state
4+	controllable atmosphere (Ar+O2, pressure), multisource, automation, fine nozzle	Substrate temperature pyrometer control, ellipsometry growth control, syringe pump dosing	Single films, multilayered structures, superlattices, interface engineering, films with controllable transition metal oxidation state

The advantage of MAD technology is the high precursor dosing accuracy delivered to the growth zone, which makes it possible to control the layer growth thickness - atomic scale precision (accuracy better than 0.01 monoatomic layer). The atomic precision layers deposition can be effectively tracked by use of ellipsometry (Figure 1 (b)).

The direct application of this feature is the layer-by-layer production of ultra-short period superlattices, layered oxides, and the heterojunctions' interface engineering. As an example, the structure having a period of 2 perovskite monolayers only is shown in Figure 2 (left image).

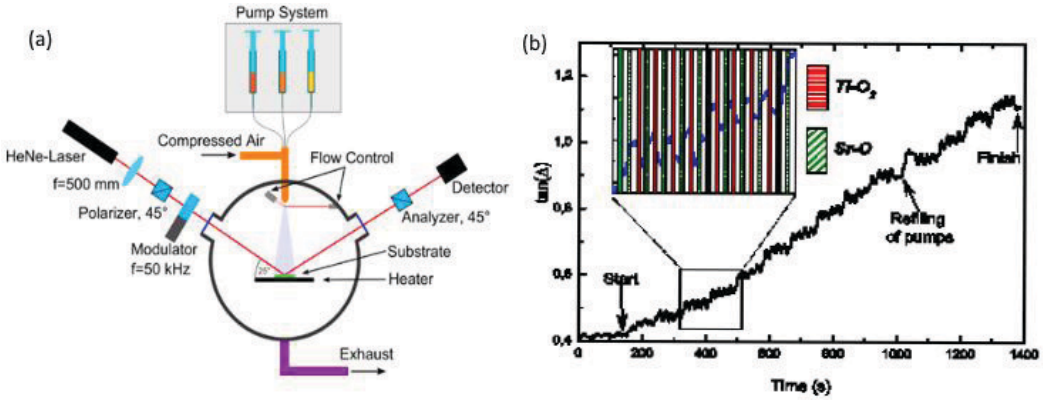


Figure 1. Metalorganic aerosol deposition system' schematics (a) and in situ ellipsometry data for phase shift angle Δ during the growth of $Sr_5Ti_4O_{13}$ on STO(100) substrate (b) as an example

Among the examples of deposition accuracy exploitation are, namely: the production of Ruddlesden-Popper structures type $A_{n+1}B_nO_{3n+1}$ with n>1 and the magnetic decoupling in manganites based heterostructures, having different magnetic properties due to Ruddlesden-Popper interfaces [5] (Figure 2 (right image)).

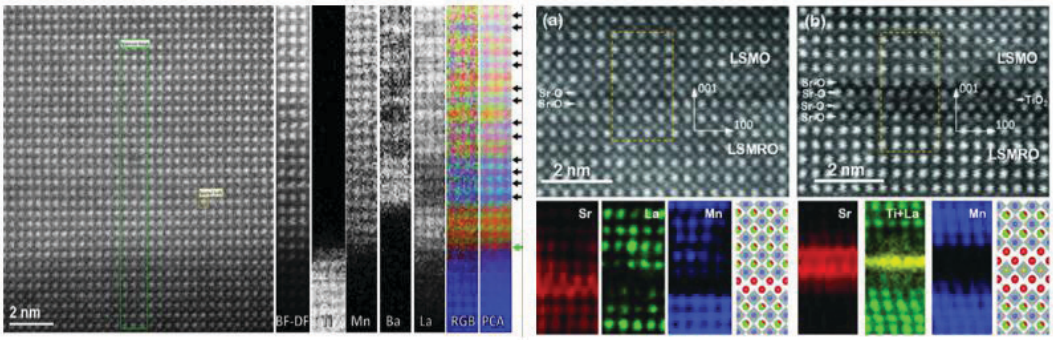


Figure 2. HAADF-STEM image and corresponding atomically resolved EELS elemental maps for Ti, Mn, Ba and La. Modulations in the Ba map of 2 unit cells thick can be clearly observed (left image). High-resolution HAADF-STEM images (top), the respective elemental EELS maps (bottom) of outlined regions and corresponding models of octahedral network of the LSMO/RPI/LSMRO trilayers with RPI consisting of a single $(SrO)_2$ (a) and a dual $(SrO)_2$–TiO_2–$(SrO)_2$ layer (b) (right image)

The 4th generation of the MAD technique addressed syntheses of the films and artificial structures based on transition metals with controllable oxidation states. An example of successful control of the growth chamber atmosphere is the single-phase VO_2 films synthesis.

Nowadays, solving the above problems makes the MAD a convenient and flexible laboratory tool for materials scientists involved in the synthesis of oxides with an accurate selection of composition and in the development of artificial oxide materials.

Furthermore, MAD, as spray assisted technique, can be scaled from laboratory samples up to industrial sized films.

Referințe:

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