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SUPPLEMENTARY INFORMATION

Low-temperature-induced crystallization of metal oxide thin films by chemical methods

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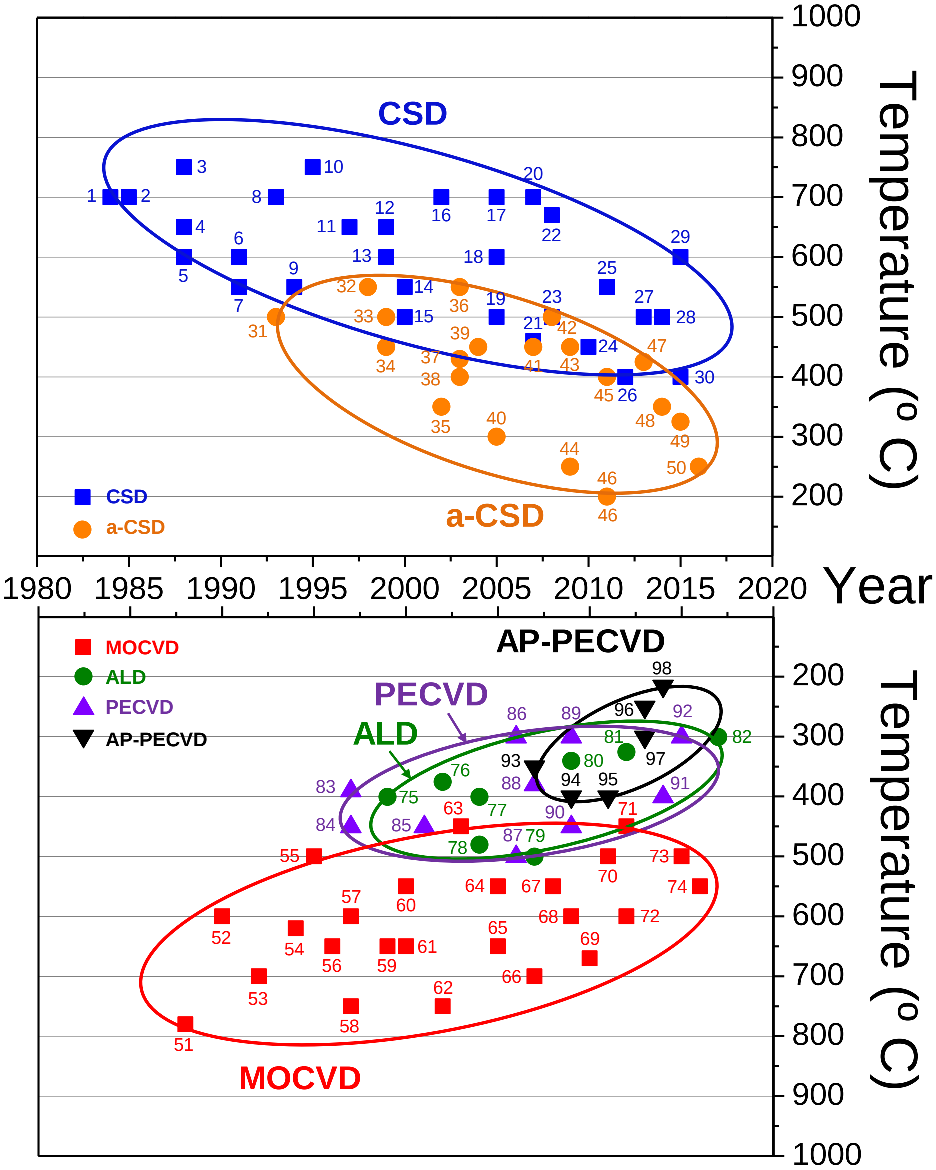

Fig. S1 List of references corresponding to the data compilation shown in Fig. 1:

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Solution method	Chemical System	Solution features	Film features and issues
Sol-Gel [1-5]	On the basis of the so-called ***sol-gel alkoxide route*** where metal alkoxides are used as reagents and alcohols are used as solvents (e.g., the toxic methoxyethanol because of its reaction with metal alkoxides, which permits to attain solutions with appropriate rheology for further deposition). Applied to precursors of ***metal oxides of transition and post-transition metal cations*** for which the synthesis of the corresponding metal alkoxide is possible, although this metal compounds are hyghly hygroscopic.	***High rates of hydrolysis and condensation reactions***. Synthesis needs to be carried out under an inert gas atmosphere and the resulting solutions are not stable in air.	***High control of the film homogeneity and stoichiometry***, control of the film properties, possible epitaxial growth on single crystal substrates, ***thermal treatments at high temperatures*** for elimination of the organics and crystallization of the oxide.
Chelate routes [3-5]	On the basis of the ***modification of the sol-gel alkoxide route by*** the incorporation of ***chelate ligands***. Metal alkoxide reagents are stabilized towards hydrolysis by the modification of their organic part with polar groups such as ether linkages, amine or keto groups. Alkaline and alkaline earth compounds containing this type of ligands can be also used as reagents (e.g., inorganic metal salts, metal carboxylates). Non-interacting liquid chemicals that not react with the metal reagents, and alcohols are used as solvents. Applied to precursors of ***metal oxides of transition and post-transition metal cations, and alkaline and alkaline earth cations***.	***Reduction of the hydrolysis and condensation reactions*** that makes possible to carry out the synthesis under air atmosphere and, in general, the resulting solutions are stable in air. Reactions in solution are complex, which result in a diminished ability to control the precursor rheology and other physico-chemical characteristics.	***Lower homogeneity and stoichiometry control*** than in sol-gel derived films, which affect functional properties. Difficulty to attain epitaxial films. ***Thermal treatments at high temperatures*** for the complete elimination of the organics and for the oxide crystallization without the formation of second crystalline phases.
Metal Organic Decomposition (MOD) [3-5]	On the basis of ***dissolving the metal reagents in the solvent***. Metal carboxylates are used as reagents. Short alkyl chain carboxylates can be dissolved in water or other polar solvents. Long, non-polar alkiyl chains lead to metal carboxylates soluble in non-polar solvents, such as xylene. Applied to precursors ***metal oxides of transition and post-transition metal cations, and low valent, ionic cations*** (e.g., Pb^{2+}, Sr^{2+}, Ba^{2+}).	***Simple solution chemistry***; no reaction among the metal reagents and the solvent, only dissolution of the former in the latter. Air-stable solutions. Less versatile than sol-gel or chelating methods.	***High thermal budgets*** for full elimination of organic residuals, which ***affect homogeneity, stoichiometry and properties***. Thermal treatments at high temperatures for the oxide crystallization and to avoid second crystalline phases.
Pechini, Citrate and Nitrate routes [3-5]	The Pechini route uses ***metal nitrates*** dissolved in ***water***, adding ***citric acid*** to chelate the metal cations. A polyhydroxy ***alcohol*** (ethylene glycol) is added to form organic ester compounds. Polymeric species are formed with molecular weights controlled by the ratio of the ethylene glycol to the citric acid. The citrate route is similar to the former, except that polyhydroxy alcohols are not used. Metal nitrates are here dissolved in water and citric acid is added to form citrate metal compounds. In the nitrate route, metal nitrates are simply dissolved in di-ionized water or alcohols. Applied to precursors of ***most metal oxides***.	***Easy solution preparation***. Air-stable solutions. Difficulty for controlling the molecular weight of the polymeric species formed in solution in the Pechini route.	***Possible cracking/porosity*** in the film during the elimination of the organics. ***Deweting*** of the substrate due to the absence of gelation and the extend of hydrogen bonding. Possible ***recrystallization*** of the starting reagents (i.e., nitrates) during drying**.** ***Relatively high annealing temperatures*** for the oxide crystallization
Aqueous Solution-Gel [3,4,6,7]	On the basis of the use of ***water as solvent*** where ***inorganic metal salts or water-soluble metal complexes*** are dissolved or reacted with water and ***chelating carboxylic acids*** like oxalic or citric acids, or other coordinating ligands like ethylenediamine. Applied to precursors of ***most metal oxides***.	***Inexpensive and environmentally friendly*** solution method. The use of any organic solvent can be avoided. Easy handling of the reagents and solutions in air and room conditions. Low carbon contamination.	***Wetting problems*** because of the water solvent that are usually solved by adding wetting agents to the solution or by increasing hydrophilicity of the substrate through a chemical cleaning process.

Molecular Precursors (e.g., aminoalkoxides, polyols derivatives, fluorinated complexes, aryloxides) [8-12]	On the basis of the ***design of the molecular structure of the precursor***. Usually, polynuclear oxo (or hydroxo) aggregates wrapped in an organic surrounding are synthesized, producing oxohydroxide clusters. These clusters can assemble multiple metal (up to six metals) and ensure high coordination numbers. Metal alkoxides, metal carboxylates, metal alkyls, metal halides, metal β-diketonates or zerovalent metals are used as metal reagents. Alcohols, diols, triols, alkanolamines or fluorinated compounds are used as solvents and metal complexing ligands. Applied to precursors of ***most metal and multi-metal oxides*** (e.g., alkaline, alkaline earth, transition, post-transition, lanthanide cations).	***Structurally designed molecular precursor solutions*** with unusual architectures and properties (e.g., molecular structure resembling a crystal structure, photosensitivity).	***Specific film properties are controlled through an appropriate design of the molecular structure of the precursor*** (e.g., photocatalysis activity, electron mobility, epitaxial growth). Thermal treatments at high temperatures because of the high molecular weight of the molecular precursor.
Polymer-Assisted Deposition (PAD) [13-15]	On the basis of the incorporation of the ***metal reagents*** (e.g., nitrates of alkaline earth cations such as Ca^{2+} or Ba^{2+}, or T^{4+} complexed with water peroxide) ***in a water solution with soluble polymers*** (e.g., polyethyleneimine) that are disolved to form a solution with a cotrolled viscosity. The polymer binds and encapsulates the metal, preventing chemical reaction and leading to homogeneous and stable solutions. Applied to precursors of ***multi-metal oxides***.	***Homogeneous metal ion distribution in the solution*** because of the binding of the metal ion to the polymer avoiding the participation of the former in undesired chemical reactions. Solutions are stable in air.	***Good control of the stoichiometry, and film uniformity and thickness***. Possible epitaxial growth. High annealing temperatures for the thermal depolymerization of the polymer species and crystallization of the oxide.
Microemulsions, Surfactants, Block-copolymer based solutions [16,17]	On the basis of the ***microemulsion synthesis*** which involves the formation of ***metal aggregates in a ternary system (water – oil – surfactant or block copolymer)***. The surfactant molecule is amphyphilic with a hydrophilic polar head and a hydrophobic non-polar tail. It forms reverse micelles consisting in water in an organic non-polar solvent where the metal reagent (e.g., metal alkoxide, metal carboxylate, inorganic metal salt) is trapped like in a reactor where the indoor synthesis of the metal oxide is produced. Applied, mainly, to ***single metal oxides***.	***Micellar solutions***, where the micelles work as micro- or nano-reactors for the oxide synthesis at room/low temperature.	***Promising method for the fabrication of self-assembled and ultrathin oxide films*** with a precise stoichiometry and high homogeneity. Crystallization occurs at ***low temperature***.
Liquid Exfoliation of layered materials (nanosheets) [18-23]	On the basis of the ***exfolation of layered crystals*** (e.g., by oxidizing agents, ion intercalation, ultrasonic waves) ***to form cystalline nanosheets of metal oxides*** (thickness of the order of a single nanometer and lateral dimensions into the micrometer range) that are subsequently ***dispersed in suitable solvents***. Applied, only, to ***layered crystals*** that can be exfoliated (strong chemical bonds in-plane and weak out-of-plane bonding, e.g., transition metal oxides: $Ti_{0.91}O_2$, Nb_6O_{17}, $Na_x(Mn_{4+},Mn_{3+})_2O_4$, TaO_3, … perovskites: Sr_2RuO_4, $LaNb_2O_7$, $SrTa_2O_7$, …)	Liquid precursors formed by ***nanosheets dispersed in a solvent***.	***Films prepared at room temperature***. Most developed for graphene and graphene oxide layers. Now in the early beginnings of application to the preparation of metal oxide films. Monolayer nanosheet films are used for the selective growth of highly textured metal oxide (ultra)thin films.

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