Recent progress in the synthesis of oxide films from liquid solutions

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This review surveys recent advances in the synthesis of oxide materials, primarily as supported thin films but also in other forms such as free-standing films, mesoporous solids, and nanostructured fibers, from liquid (primarily aqueous) solutions. New studies using chemical bath deposition (CBD), liquid phase deposition (LPD), and successive ion layer adsorption and reaction (SILAR) to produce single- and multi-component oxide films, and the role that functionalized substrates can play in these deposition techniques, are surveyed. This review highlights significant new insights that have been gained in areas such as: nucleation and growth kinetics as they pertain to film growth in oxide systems; multicomponent films; the roles of polymers and other organic additives on the film deposition mechanism; and fabrication of patterned films and other advanced material morphologies.
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1. Introduction

Several recent trends in materials chemistry have contributed to increased interest in the synthesis of oxide materials from liquid solutions at low temperatures. The quest for new materials with tailored structures on the nanometer scale has driven much creative work in controlling the feature sizes of materials on the molecular and mesoscale level.[1] Increased understanding of biomineralization processes suggests strategies for achieving exquisitely controlled hierarchical structures over multiple length scales in synthetic materials.[2] The pursuit of more environmentally benign manufacturing favors less energy-intensive materials processing and reduced use of volatile organic precursors. Prior development of solution routes for non-oxide films[3),4)] has provided insights into the mechanisms underlying aqueous chemical deposition techniques. These trends, as well as intrinsic benefits of solution processing routes (e.g. low capital equipment cost, processing compatibility with low-temperature materials such as polymers, and the ability to infiltrate porous substrates) have made low-temperature, liquid processing of oxides in various functional forms a vigorous area of study around the world.

This brief survey emphasizes work published since the reviews by Niesen and De Guire[5] in 2001 and by Gao and Koumoto[6] in 2005. The surveys by Hodes,[3),4)] while primarily devoted to nonoxide semiconductor films, also contain useful summaries of oxide films. The scope here is restricted to oxide materials (as opposed to carbonates, phosphates, other chalcogenides, etc.), synthesized almost exclusively from aqueous media at temperatures primarily between 0 and 100°C, in a functional form (films, fibers, mesoporous solids, etc.). Exciting progress has been achieved in hydrothermal, electrochemical, ultrasonic and optical routes, but space does not permit addressing them here. The present review does not aim for exhaustive coverage of the topic, but instead will highlight some of the significant advances that have marked the field even in the short time since 2005.

Most depositions of oxide films from liquid solutions at low temperatures fit into one or more of the following categories of techniques:[5]

- **Chemical bath deposition (CBD):** techniques that produce a solid film in single or repeated immersions, usually by adjusting pH, temperature, or composition of the source solution to control the kinetics of formation of the solid. CBD is the most general approach — applicable to both oxide and chalcogenide films — and the oldest: Hodes[4] cites a report from 1869 describing sulfide layers deposited from thiosulfate solutions of copper, lead and antimony salts. Variations on CBD include photochemical deposition, deposition assisted by applied fields, ferrite plating, use of functionalized surfaces, and liquid flow deposition. **Table 1** summarizes several of the reports on CBD published mostly since 2005.
- **Liquid phase deposition (LPD):** formation of oxide thin films from an aqueous solution of a metal-fluoro complex MF_n^{m-n} which is slowly hydrolyzed by adding water, boric acid (H_3BO_3) or aluminum metal. Although the approach is a subset of CBD as defined here, the great variety of oxides to which this technique has been applied, notably by Deki (see, e.g.[14),15),17),27)]), and the unique combination of fluoride precursors and a fluorine scavenger warrant separate mention. This technique was first described in a patent[28] on producing titania films on glass in 1984. Table 1 summarizes several of the reports on LPD published largely since 2005.
- **Successive ion layer adsorption and reaction (SILAR):** film growth through the use of repeated immersions of the substrate alternately into solutions of a metal salt solution, then a hydrolyzing solution. This technique was first reported for sulfides[29] and independently for Cu(I)[30] and Zn(II)[31] oxides in the mid-1980s. Tolstoy[32] recently reviewed the potential applications of SILAR in gas sensing,

Table 1.   Deposition Parameters and Physical Characteristics of Some Oxide Films Deposited by Chemical Bath Deposition (CBD and Liquid Phase Deposition (LPD) Since 2005, on Substrates not Pre-treated with Self-assembled Monolayers

system		solution				form as dep'd*	annealing T (time) ºC (h)	growth rate† (nm/h)	maximum thickness (nm)	ref
oxide	substrate	precursors	additives	pH	T (ºC)					
CBD										
CeO_2	silica glass	$Ce(CH_3COO)_3$	$KClO_3$	n.r.	30–50	C	n.a.	2.5	60	7
Cu_2O	glass	$CuSO_4$	$Na_2S_2O_3$	n.r.	50–85	C	250–425 (0.5–1.5)	n.s	4×10^2–5×10^2	8
In_2O_3	glass	$In(NO_3)_3 \cdot nH_2O$	H_2O_2, NH_3	n.r.	50–70	$In(OH)_3$	300		180	9
MnO_2	TiO_2-coated SiO_2 glass	$MnCl_2 \cdot 4H_2O$	$NaBrO_3$	4.8–5.3	50–70	C	n.a.	42	1×10^3	7
TiO_2	Si, TCO glass, PET	H_2TiO_3	NH_3, H_2O_2, HNO_3	1–2	20–95	NC	500 (0.5)	33–60	3×10^3	10
ZnO	ITO glass	$ZnCl_2$	$C_6H_{12}N_4$, NH_3	n.r.	95	C	n.a.	200	$1 \times 10^{4\,(1)}$	11
ZnO	ITO glass	$Zn(NO_3)_2 \cdot 6H_2O$	$C_6H_{12}N_4$	3–7	95	C	n.a.	2000	$8 \times 10^{3\,(1)}$	12
ZnO	glass	$Zn(NO_3)_2 \cdot 6H_2O$	$C_6H_{12}N_4$	3–7	95	C	n.a.	1000	$1 \times 10^{4\,(1)}$	13
LPD										
$(Cu,Fe)_3O_4$	glass	FeOOH, $CuCl_2$, $Cu(NO_3)_2$	$NH_4F \cdot HF$, H_3BO_3	acidic	30	NC	600 (1)	n.r.	n.r.	14
SnO_2	Si	SnF_2	H_2O_2, H_3BO_3	1.9	30, 50	C	400, 600 (2)	38	950	15
TiO_2–SiO_2	glass	$(NH_4)_2TiF_6$, $(NH_4)_2SiF_6$	$NH_4F \cdot HF$ H_3BO_3	n.r.	35	C	n.a.	n.r.	n.r.	16
TiO_2, SnO_2, β-FeOOH	liquid-liquid interface	$(NH_4)_2TiF_6$ $SnO_2 \cdot nH_2O$, FeOOH	H_3BO_3	acidic	30	TiO_2: anatase	n.a.	–	1×10^3	17
TiO_2	latex spheres	$(NH_4)_2TiF_6$	H_3BO_3	2.9 or 3.9	50	TiO_2: anatase	n.a.	18	425	18
TiO_2	glass, ITO on glass	$(NH_4)_2TiF_6$	$Al(NO_3)_3$, $FeCl_3$, H_3BO_3	2 –2.8	80	PC	500 (3)	85–150	250–450	19
TiO_2	graphite	$(NH_4)_2TiF_6$	H_3BO_3	6	22	anatase	500 (1)	n.r.	n.r.	20
MB–TiO_2	glassy carbon	$(NH_4)_2TiF_6$, MB	H_3BO_3	4–8	25	n.r.	n.a.	4	80	21
DA–TiO_2	ITO on Glass	$(NH_4)_2TiF_6$, DA	$Al(NO_3)_3 \cdot 9H_2O$	2	80	C	n.a.	110	5×10^2	22
MB–TiO_2	ITO on Glass	$(NH_4)_2TiF_6$, MB	H_3BO_3,	2.8	80	C	n.a.	105	5×10^2	23
$ZnAl_2O_4$	chromic acid treated glass	ZnO	Al foil	acidic	n.r.	C	n.a.	2	$30^{(1)}$	24
ZrO_2:Tb	Si, glass	H_2ZrF_6, Tb_4O_7	HCl, Al foil, DTPA	acidic	30	NC	500–900 (2)	8	2×10^2	25
ZrO_2:Eu	SnO_2 inverse opal	H_2ZrF_6, Eu_2O_3	HCl, Al foil, DTPA	acidic	n.r.	n.r.	n.a.	11	132	26

Abbreviations — n.r.: not reported; n.a.: not applicable; ITO: indium tin oxide; TCO: transparent conducting oxide-coated; PET: poly(ethylene terephthalate); MB: methylene blue; DA: dopamine; DTPA: diethylenetriaminepentaacetic acid.
*) form of film, as deposited. C: crystalline; NC: non-crystalline; PC: partially crystalline.
†) If no growth rate was reported, this value is an average growth rate, computed as maximum thickness divided by deposition time.
1) Height of nanorods.

photovoltaics, electronics, and lighting applications. **Table 2** summarizes several of the reports on SILAR published since 2005.

• **Electroless deposition:** an electrochemical technique entailing a change of oxidation state of a solvated species and catalyzed deposition at a "sensitized" substrate without use of externally imposed sources of electrical energy. This technique is an adaptation of electroless plating techniques that are widely used for depositing metal films. In a recent example,[43] films of β-FeOOH, Fe_3O_4, or Fe were deposited on amine-functionalized Si that had been immersed in a Pd salt solution for sensitization; dimethylamine borane complex (DMAB, $(CH_3)_2NHBH_3$) in the deposition liquid served as the reducing agent.

In all of these techniques, the role of the substrate and its interactions with the deposition liquid can be critical in determining the physical characteristics of the film — e.g. adhesion, density, continuity, thickness, roughness — and even whether a film will form at all. One of the ways used to control the surface chemistry of the substrate has been pre-treatment with organic self-assembled monolayers (SAMs). (For earlier reviews, see.[5),6)] **Table 3** summarizes several studies since 2005 that have featured the use of SAMs to functionalize the substrate surface before deposition.

Many of the materials discussed in this review have never seen a temperature above 100°C. As a result, they tend to be mechanically weak relative to fired ceramics. For example, Cho and co-workers[56] report a modulus of elasticity of 30 GPa and an indentation hardness of 1 GPa for a CBD ZrO_2 film on a phos-

Table 2.   Deposition Parameters and Physical Characteristics of Oxide Films Deposited by Successive Ion Layer Adsorption and Reaction (SILAR) Since 2005, on Substrates not Pre-treated with Self-assembled Monolayers. (PSS: Sodium Poly(Styrenesulfonate); PEI: Poly(Ethyleneimine); Other Abbreviations are the Same as in Table 1.)

system			solution				form as dep'd*	annealing T (ºC)	growth rate (nm/cycle)	maximum thickness (nm)	ref.
oxide	substrate	salt	additives	pH	T (ºC)						
$(Ce,Gd)O_{2-x}$	silicon,	$Ce(NO_3)_3 \cdot 6H_2O$	NH_4OH	acidic	n.r.	C	800	6.4	37–150	33
$(Zr,Y)O_{2-x}$, ZrO_2	SiO_2	$ZrOCl_2 \cdot 8H_2O$,	NH_4OH	acidic	n.r.	C	600	5.4	19–110	
		$YCl_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 5H_2O$,					600	5.2	61–94	
$(Zr,Y)O_{2-x}$	silicon, SiO_2	$ZrOCl_2 \cdot 8H_2O$, $YCl_3 \cdot 6H_2O$	NH_4OH	acidic	n.r.	C	600	5.4	100	34
ZrO_2	silicon, SiO_2	$ZrCl_4$, Zr acetate	PSS, PEI	1.32–4.14	n.r.	C	600	n.r	40	35
ZrO_2	silicon	$Zr(SO_4)_2$	NaOH	n.r.	24–26	n.r.	n.a.	0.62	31	36
ZnO	ITO glass	$Zn(NO_3) \cdot 6H_2O$	$C_6H_{12}N_4$	3–7	95	C	hydrothermal	2000	$8 \times 10^{3\,(1)}$	12
ZnO	glass	$Zn(SO_4)$	$NH_3 \cdot H_2O$	n.r.	90	C	n.a.	n.r.	n.r.	37–39
Sn doped ZnO	glass	$Zn(SO_4)$, Na_2SnO_3	NaOH	n.r.	95–98	C	350–650	1.8–2.5	200–450	40
ZnO	glass, silicon	$Zn(SO_4)$	NH_3	n.r.	95	C	n.a.	30	300	41
$Sn_{16}(OH)_x PW_{19}O_y$	quartz, silicon	$SnCl_2$	$H_3PW_{12}O_{40}$	2	n.a	C	600	n.r.	200–400	42

*) form of film, as deposited. C: crystalline; NC: non-crystalline; PC: partially crystalline.

Table 3.   Deposition Parameters and Physical Characteristics of Oxide Films Deposited from Aqueous Solutions Since 2005, on Substrates Pre-treated with Self-assembled Monolayers. (PVP: Poly(Vinyl Pyrrolidone); Other Abbreviations are the Same as in Table 1.)

system			solution				form as dep'd*	annealing T (time) ºC (h)	growth rate (nm/h)	maximum thickness (nm)	ref.
oxide	substrate	functional group	salt	additives	pH	T (ºC)					
In_2O_3	Si	$-SO_3H$	$InCl_3 \cdot 4H_2O$	—	n.r.	60	$In(OH)_3$	400 (2)	40	4×10^2	44
TiO_2	Si	$-CH_3$, $-NH_2$, $-SO_3H$	$Ti(SO_4)_2$	H_2O_2	1.2	80	anatase	500	7.5 –9	2.5–3	45
TiO_2	Si	$-SO_3H$	H_2TiO_2	HCl	n.r.	60	anatase	n.a.	65	4×10^2	46
$TiO_2-V_2O_5$	Si	$-SO_3H$	$TiCl_4$, H_2O_2, NH_4VO_3,	HCl	n.r.	60	$(Ti,V)O_2$	n.a.	14	84	47, 48
$TiO_2-V_2O_5$	Si	$-NH_2$	HVO_3, $(NH_4)_2TiF_6$	H_3BO_3	2.5–3.6	45	NC	n.a.	62	1.5×10^3	49
$TiO_2-V_2O_5$	Si	$-N^+(CH_3)_3$	HVO_3, $(NH_4)_2TiF_6$	H_3BO_3	2.5–3.6	45	NC	n.a.	92	2.2×10^3	49
V_2O_5	Si	$-NH_2$	HVO_3	HCl	1.2–3.0	45, 65, 85	$V_2O_5 \cdot H_2O$	n.a.	220	1.6×10^3	50
V_2O_5	Si	$-N^+(CH_3)_3$	HVO_3	HCl	1.2–3.0	45, 65, 85	$V_2O_5 \cdot H_2O$	n.a.	1100	8×10^3	50
Y_2O_3:Eu	Si	$-NH_2$	$Y(NO_3)_3 \cdot 6H_2O$ $Eu(NO_3)_3 \cdot 6H_2O$	urea	5.5	77	NC	800 (1)	70	1×10^2	51
ZnO	Si	$-CH_3$, $-NH_2$, $-C_6H_5$	$Zn(COOCH_3)_2$	NH_3	7.0, 7.5, 8.9	50	C	n.a.	n.r.	n.r.	52
ZnO	Si	$-SO_3H$	Zn acetate	PVP	†	60	C	n.a.	16	5×10^2	53, 54
ZrO_2	Si	$-SO_3H$	$Zr(SO_4)_2 \cdot 4H_2O$	HCl	n.r.	70	C	500–800 (2)	30	45–180	55
ZrO_2	Si	$-PO(OH)_2$	$Zr(SO_4)_2 \cdot 4H_2O$	HCl	n.r.	70–90	$t-ZrO_2$	n.a.	2	50	56

*) form of film, as deposited. C: crystalline; NC: non-crystalline; PC: partially crystalline.
†) Solution was methanol-based.

phonate SAM, compared to 205 and 11.8 GPa, respectively, for bulk sintered zirconia. As a result, applications for these solution-deposited coatings in mechanically aggressive environments are expected to be limited. Mechanical performance presumably improves on firing, but resorting to high-temperature processing diminishes some of the key advantages of liquid deposition routes.

On the other hand, applications such as solar cells, luminescent materials, photocatalysts, sensors, and transparent conducting films, in which either mechanical strength is not paramount or the film can be protected against mechanical damage, remain attractive. Indeed, two oxides that qualify for many of these applications, TiO_2 and ZnO, have emerged as the most widely studied oxides deposited by the techniques reviewed here. These materials therefore demonstrate the range of capabilities of liquid deposition techniques for oxides in general, from novel morphologies and patterning to prospective applications, and have also provided much of the advanced understanding of deposition mechanisms that has been obtained in the last few years.

2. New developments

2.1 Morphologies

As familiarity with and understanding of the deposition methods have advanced, the forms of the synthesized materials have expanded beyond thin films. For example, Gao et al. deposited nanorods of *c*-oriented, wurtzite-structure ZnO[11] and nanoporous films of TiO_2[10] by CBD routes after first depositing a dense "seed" layer of the respective oxide. The high surface areas of the nanostructured films are attractive for dye-sensitized solar cells. To form the ZnO nanorods, it was necessary to add a small amount of ammonia to the $ZnCl_2$-hexamethylenetetraamine solutions. To obtain the porous titania films, solution conditions were controlled to bring about evolution of oxygen gas from acidic solutions of titanic acid, hydrogen peroxide, and ammonia. These studies show the sophisticated interplay of solution chemistry, film morphology, and application that marks recent advances in functional oxide film deposition from aqueous solutions.

In a unique adaptation of the LPD technique, Deki and co-workers[17] formed films of TiO_2, SnO_2, or β-FeOOH at a liquid-liquid interface, i.e. at the interface between the deposition liquid and a layer of *n*-hexane, cyclohexane, or benzene on top of the deposition liquid. Films grew up to 1 μm thick. The authors attributed the localization of film growth at the interface to increased supersaturation of the LPD precursors there, as water molecules would be relatively repelled by the hydrophobic nature of the top liquid layer. If this inference is correct, the approach should work as well on a variety of CBD systems and suggests a simple way to produce free-standing films of virtually any of oxides producible using e.g. CBD or LPD (Table 1; refs.[5),6)]).

In another example of materials deposition at a non-solid interface, Shyue and De Guire[57] used micelles of surfactants (cetyltrimethylammonium bromide (CTAB) or hexadecylamine (HDA)) as "substrates" to control the morphology of TiO_2–V_2O_5 mesoporous powders. The effectiveness of these materials as heterogeneous partial oxidation catalysts for lactic acid scaled with the surface area and the vanadium content of the powders. Surface area in turn could be controlled by the choice of surfactant and the solution composition, illustrating how the deposition process could be engineered to achieve a desired level of performance in a functional oxide material synthesized via low-temperature deposition.

Whereas the mesoporous materials of Shyue and De Guire

formed on the outside of the surfactant micelles, Nakata et al.[58] used a reverse micelle approach, synthesizing nanoparticles of monoclinic VO_2, orthorhombic Ta_2O_5, and Sn and Nb oxides of unidentified structures on the inside of micelles of Triton or cyclohexanol in hexane via LPD at 30°C.

Using polymer (usually latex or polystyrene) spheres of uniform size as substrates for deposition of oxide films takes advantage of the low temperature of these deposition processes. Lipowski et al.[53),54)] used their route for deposition of ZnO (discussed in more detail below) to produce nanocrystalline coatings 160 nm thick on sulfonate-functionalized polystyrene spheres. The polymer could be dissolved or pyrolyzed away, leaving intact hollow ZnO shells. Strohm and Löbmann[18] studied the effects of a wide variety of surfactant and polyelectrolyte surface treatments of such spheres on LPD of TiO_2 (anatase). While the deposition was very sensitive to the surface functionalization of the films, electrostatic interactions between the substrate and the particles did not appear to play a decisive role in the film deposition. Aoi et al.[59] used LPD to deposit β-FeOOH on PS spheres, which after pyrolysis in vacuum at 400°C for 2 h produced magnetic Fe_3O_4 hollow spheres, ~900 nm in diameter with wall thicknesses of ~60 nm. Mizuhata et al.[26] took this approach a step further, by first using an assembly of PS spheres ~150-nm diameter as a template for deposition of a "reverse opal" of SnO_2 via LPD. After burnout of the spheres, they then infiltrated the resulting spherical voids with Eu-doped ZrO_2, with a view toward photoluminescent and optoelectronic applications.

One of the attractive features of liquid deposition techniques is the ability to coat porous structures and surfaces with complex topographies via infiltration by the deposition liquid. For example, Mizuhata et al.[27] utilized this capability in two ways. One way was to make polymer molds of three-dimensional architectures that had been produced in Si via deep reactive-ion etching (RIE), and then infiltrate these molds with LPD precursors for SnO_2, TiO_2, or ZrO_2 to produce replicas of the original Si structures. The second approach was to coat the Si structures directly with conformal films, 100–200 nm thick, of the LPD oxides. Pillars 6 μm tall, 0.5 μm in diameter, and spaced 0.5–1 μm apart were coated uniformly with adherent oxide films ~100–200 nm thick. Such structures are of interest for photonic crystals, data storage, and field emission devices.

To counter the relative fragility of the as-deposited films, some investigators have explored the deposition of laminated multilayer films, alternating oxide layers with organic layers. In this approach, researchers hope to replicate (at least to some extent) the remarkable ruggedness of biominerals such as nacre, whose structure consists of crystalline layers of $CaCO_3$ (aragonite) between thin protein-based layers comprising ~5 vol% of the material. Burghard et al.[46] produced laminated titania (120 nm)-polyelectrolyte (25 nm) composites. Three different polyelectrolytes were used — sodium poly(styrene sulfonate) (PSS), polyethyleneimine (PEI), and poly(allylaminehydrochloride (PAH) — to form multilayers composed of (PEI/PSS)(PAH/PSS). In nanoindentation measurements, films with three pairs of such layers on silicon showed hardness values 15% higher than a liquid-deposited TiO_2 film of the same thickness (1.75 GPa vs. 1.5 GPa).

In similar work on ZnO (120 nm)-polyelectrolyte (9 nm) laminate films,[60] this group found that the laminated films were ~25% harder (2.1 GPa vs. 1.7 GPa). Their polyelectrolyte layers consisted of PSS, poly-L-glutamic acid (PLGA) and poly-L-lysine hydrobromide (PLL).

2.2 Multicomponent films

Table 1 cites several examples of solid solutions and ternary compounds, but these continue to be in the minority in the literature. The task of obtaining complex oxides is made easier for doped materials or solid solutions, i.e. when a specific cation stoichiometry is not required, and if the two cations have similar precipitation behavior at a given temperature and pH. These conditions apply, for example, to the LPD synthesis of $(Cu,Fe)_3O_4$ by Deki et al.[14] If the cations have different precipitation tendencies, a complexing agent can be used to slow the deposition kinetics of the more readily hydrolyzed species. For example, Shyue and De Guire[61] deposited amorphous $TiO_2–V_2O_5$ films from LPD-type solutions onto silicon wafers treated with amine and alkylammonium-functionalized SAMs. They reported that oxalic acid chelates both titanium and vanadium, but preferentially vanadium. The situation with lactic acid was more complex, as the lactate ion partially reduced V^{5+} to V^{4+}, which in turn catalyzed deposition of pentavalent vanadium in the film. The composition of the films could be empirically adjusted over wide ranges by controlling the Ti/V ratio and complexant concentration. Hoffmann et al.,[47,48] using CBD, succeeded in depositing crystalline $(Ti,V)O_2$ films on Si with and without sulfonate SAMs.

The sequential nature of the SILAR technique circumvents some of the incompatibilities in deposition conditions that may exist between two components of a desired multicomponent film. Nevertheless, the deposits usually still need heat treatment to yield the desired crystalline phase. Using SILAR, Arcot and Luo[33,34] deposited amorphous hydroxylated films that crystallized to gadolinium-doped ceria and yttria-doped zirconia on annealing. Shishiyanu et al.[40] deposited Sn-doped ZnO films using a similar approach. Tolstoy et al.[42] formed crystalline hybrid $Sn_xO_yH_z–H_xPW_yO_z$ films from amorphous SILAR-deposited films.

In an example of depositing a crystalline stoichiometric compound directly from solution, Kumar et al.[24] synthesized $ZnAl_2O_4$ spinel films on chromic acid-treated glass by reacting solid ZnO and Al foil in HF solutions. This in essence created an LPD solution by dissolving the solid precursors in the HF.

2.3 Film formation— nucleation and growth theory

The review of 2001[5] discussed two limiting cases of film growth mechanisms from supersaturated liquid solutions: heterogeneous nucleation and growth of the solid on the substrate; and formation of particles in the bulk solution, followed by attachment to the substrate. The widely studied case of apatite deposition from simulated body fluid (SBF) pioneered by Kokubo[62] appears to be a clear case of heterogeneous nucleation and growth:[63] the SBF alone is stable against precipitation for months. Conversely, the growth kinetics of tin oxide films via liquid flow deposition clearly indicated a particle attachment mechanism was at play.[64] Several recent studies of film deposition have invoked a particle attachment model to account for the observed films.[18,54,56,65] Still, it can be difficult by post-deposition examination to infer unambiguously the mechanism by which any particular film has formed. Furthermore, as is becoming increasingly clear with recent detailed studies of film formation mechanisms, the overall deposition process is often more complicated than either simple heterogeneous nucleation or particle attachment. Intermediate amorphous solid phases sometimes play critical roles, as in the apatite films cited above and in zinc oxide films deposited from methanol solutions in the presence of poly(vinyl pyrrolidone) (see below). Using an example from

nonoxide films, cadmium hydroxide was identified in the 1970s to be an intermediate phase in the CBD of cadmium sulfide films.[66]

Regardless of the specific deposition mechanism, the degree of supersaturation of the solution plays a central role in film formation. Supersaturation is most often controlled by the concentration, pH, and temperature of the solution.[56,67,68] When film growth occurs by particle attachment, the degree of supersaturation dictates the size, population, and rate of formation of the particles making up the film. These effects lend themselves to quantitative analysis using classical nucleation and growth theory. Such an analysis was carried out by Cho and co-workers[69] on the nucleation and growth kinetics of titania nanoparticles during CBD from supersaturated solutions of $TiCl_4$ and HCl. The particle sizes were measured using dynamic light scattering (DLS) as a function of time and solution conditions (pH, Ti concentration, and temperature). SEM and TEM images of the particles and of films deposited from the precipitating solutions showed good agreement with the particle size data from DLS. This study yielded values for fundamental parameters such as the interfacial surface energy between the titania nanoparticles and the deposition solution ($0.168 \, J \, m^{-2}$ at 70°C) and the critical nucleus size (0.46–0.54 nm). This work lays a foundation for further systematic studies of other oxide deposition systems and for relating solution conditions to film growth rates and microstructures.

2.4 Effects of organic additives

One of the most important developments in this field in recent years has been the recognition and exploitation of the role that organic additives in the deposition liquid can play in controlling the morphology of the depositing film. Tian and co-workers[70,71] showed that adding sodium citrate to a solution of zinc nitrate and hexamethylene tetraamine changes the morphology of growing ZnO crystals from long hexagonal rods (their natural habit) to flat hexagonal platelets. They attributed this to preferential adsorption of the citrate ion to the (0001) faces of the wurtzite-structure ZnO crystals. Through seeded film growth with controlled amounts of added citrate, they produced c-oriented ZnO films analogous in structure to nacre. Imai and co-workers[72] reported a similar "planarizing" effect when tartaric or maleic acid was added to zinc sulfate/ammonium chloride solutions (9.0 < pH < 10.5). In contrast acetic, salicylic, fumaric, and succinic acids had no effect on the morphology of the ZnO crystals. They associated this effect to the presence of multiple carboxylate groups on the same side of the added organic molecule: e.g., maleic acid is the *cis* isomer of the diacid $C_4H_4O_4$, whereas fumaric acid is the *trans* isomer. They observed a "miniaturizing" effect — nanoscale, more equiaxed ZnO crystals — by adding polyacrylic acid (PAA, which has carboxylate side groups) or the surfactant sodium dodecyl sulfate. They attributed this to strong, crystallographically non-selective adsorption of these molecules on the growing crystals, and to spatial confinement of the growing crystals by the additives. A mosaic structure was observed with the addition of the bulky, monocarboxylic acid dye molecule eosin Y, which was attributed to its weak, non-selective adsorption on the ZnO crystals.

Bill, Hoffmann, Lipowski and co-workers[53,73,74,75,76] established that β-cyclodextrin, poly(ethylene glycol) (PEG), and poly(vinyl pyrrolidone) (PVP) suppress the tendency for ZnO to form either hexagonal platelets or elongated rods, instead promoting the formation of equiaxed particles that pack efficiently into dense, uniform films. These results are similar to the effects

of PAA on ZnO morphology reported by Imai et al..[72] Gerstel et al.[77],[78] surveyed the effects of 8 amino acids and 21 dipeptides on the morphology of ZnO films. The CBD solution consisted of zinc nitrate and hexamethylene tetraamine in equimolar ratios and concentrations of 15 or 30 mmol at 60°C (similar to the solution of Tian et al.[70],[71]), with the Zn:biomolecule ratios ranging from 1:1 to 8:1 and $5.9 < pH < 7.1$. Overall, the morphologies ranged from sponges, honeycombs, ribbons, spheres, sheets, and cubes, to hexagonal platelets. In the presence of glycine (Gly) or Gly–Gly, patchy deposits of hexagonal ZnO platelets or sponge-like structures were observed, whereas layered basic zinc salts as ribbons or nets formed in the presence of glutamic acid (Glu), Glu–Glu, Glu–Gly or Gly–Glu. The amino acids and dipeptides with a complexing group (His, Trp, Cys) or a second carboxylic acid group (Asp, Glu) showed the greatest ability to alter the morphology. This effect of multiple carboxylic acid groups again is consistent with the observations of Tian et al.[70],[71] and Imai et al.[72] On the other hand PAA (a polycarboxylic acid), PVP (with amide side groups), PEG (a polyether), and β-cyclodextrin (a large cyclic hydrocarbon with multiple ether and alcohol groups) all had similar effects on the morphology of ZnO films as described above, although the functional groups and structures of these molecules are quite different. This indicates that further study is needed to provide a more detailed understanding of the interactions between organic molecules and the surfaces of growing inorganic crystals.

The role of an organic additive may not just consist of controlling the growth rates of certain crystal faces. Lipowski et al.[76] elucidated the role of a transient, intermediate amorphous phase in ZnO film growth in the presence of PVP, using transmission electron microscopy (TEM), X-ray diffraction (XRD), quartz crystal microbalance (QCM) measurements, atomic force microscopy (AFM), mass spectroscopy, nuclear magnetic resonance (NMR), thermal analysis, particle size analysis, and electrical conductivity measurements. In the absence of PVP or at PVP volume fractions $\phi < 0.04$, rod-like nanocrystalline ZnO formed almost immediately on adding base to the Zn acetate-methanol solution, yielding large, disordered ZnO crystalline clusters that did not form continuous films. At higher PVP concentrations, needle-like amorphous nanoparticles that incorporated PVP were detected. These amorphous particles presumably reduced the degree of supersaturation of the solution, suppressing the rapid formation of the initial rod-like crystals. The amorphous particles dissolved in 1–2 h, followed by the formation of ZnO nanocrystals. These nanocrystals then aggregated into either fractal assemblages or into compact clusters (depending on the PVP concentration), a process attributed to depletion forces that exclude the polymer from the space between the oxide nanocrystals. These aggregates formed continuous films, with the maximum thickness, smoothness, and (002) texturing occurring at $\phi = 0.10$. At $\phi \geq 0.20$, no particles (and no films) formed. The amorphous particles therefore appear to function as both a reservoir and gradual-release source of Zn ions, promoting a more controlled crystallization process. The authors cited numerous instances in which noncrystalline intermediate solid phases are observed both in synthetic crystallization in biomineralization processes.

2.5 Patterned films

An attractive feature of liquid deposition routes, when coupled with the use of surface functionalization strategies such as the use of SAMs, is the ability to distribute (i.e., pattern) the functionalization spatially prior to deposition, so as to control where the film will deposit. Patterned functionalization can be achieved through microcontact printing, or by shining UV light through a photomask either to alter the functional group itself or to cleave the adsorbed species from the surface. In contrast to standard photolithography, this permits patterning of the oxide to be achieved without use of photoresists and without a subtractive step such as etching to remove oxide material that has already been deposited.

The 2005 review by Gao and Koumoto[6] extensively surveyed this topic, and this group has continued to make contributions to this area. For example, ZnO was deposited via CBD from zinc acetate solutions (see Table 3) on photopatterned methyl-, phenyl-, and amine-terminated SAMs on single-crystal silicon.[52] Deposition occurred preferentially on the hydrophobic, methyl-terminated regions; this was attributed to adsorption of acetate ions to the growing zinc crystals, leading to hydrophobic attraction between the methyl groups on the adsorbed acetate ions and the SAMs. Lines of 3 μm width and 7 μm apart were reproduced with excellent resolution. An Eu-doped, amorphous yttrium basic carbonate preferentially deposited on amine and methyl-terminated SAMs and on as-received silicon wafers, but not on a highly hydrophilic UV-treated silicon wafer nor on regions where a SAM had been removed by UV irradiation.[51] Feature sizes as narrow as 10 μm were reproduced. Heating to 600 or 800°C for 1 h transformed the patterned film to mechanically adherent, single-phase, strongly photoluminescent, Eu-doped Y_2O_3, a common red phosphor.

3. Summary and prospects

The synthesis of functional oxides from liquid solutions has expanded rapidly since the first comprehensive review of the field was published in 2001. Among the most notable advances are:

(1) Use of polymer and other organic additives in the deposition solution to control the morphology of the oxide material. These strategies extend to the use of biomolecules such as amino acids, and represent a rich new frontier of research not only for oxide material synthesis but also for biomedical applications of oxide materials and greater understanding of biomineralization processes.

(2) Synthesis of more complex structures at the nano-, meso-, and microscopic levels, such as nanotubes, hollow spheres, multilayer organic-inorganic laminates, and patterned oxide films.

(3) More detailed understanding of the mechanisms by which these materials form, e.g. via intermediate amorphous phases.

Along with the attractive features of these routes, such as the low temperatures and simple hardware used, significant limitations exist as well. It remains challenging to synthesize multi-component materials (e.g. tin-doped indium oxide or barium titanate) whose individual components precipitate at widely differing pH. To realize the full scope of the properties offered by oxides, the materials synthesized from liquids often must be heated at moderately high temperatures, somewhat negating the advantages of the initial low-temperature processing.

Nevertheless, as the versatility of these solution routes becomes better recognized, it can be hoped that a breakthrough application for solution-derived oxide materials, analogous to the critical role played by CdS films in photovoltaic devices, will draw more widespread attention to the potential advantages of these approaches.

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