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Methods of Fabricating Thin Films for Energy Materials and Devices

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Abstract

With the continued miniaturization of the electronic devices applicable in our daily lives, thin films of various functional materials used in such devices are increasingly preferred over the traditional bulk components. Various gas-phase methods have been found to be capable of depositing thin films of good quality and are well-established across the coatings' industry. However, they are associated with ultrahigh vacuum systems and complicated and expensive instrumentation, and may involve toxic or corrosive chemical precursors. Alternative fabrication methods such as the electrospray deposition, the sol-gel method, and the molecular precursor method have been devised and represent active research areas. The molecular precursor method is relatively new. However, it has been found to be capable of effectively fabricating thin films of various metal oxides and of metals. In this chapter, some methods employed in the fabrication of the thin films are discussed in detail. The ease of practical application and relative cost-effectiveness associated with each method, the quality, and type of the fabricated thin films are also discussed. Based on the recent results by the present authors, the fabrication and characterization of a highly conductive and well-adhered thin film of metallic copper by using the molecular precursor method are presented.

Keywords: thin films, active materials, efficient electrical conductors, gas phase processes, liquid phase processes

1. Introduction

The use of highly functionalized thin films in various electronic devices has made life comfortable [1] and this is due to the enhanced functional properties of materials at the nano-scale level. At present, the miniaturization of various electronic devices is inevitable as the electronics industry looks at manufacturing thinner and lighter devices [2], in addition to reduced power consumption. For example, in secondary lithium-ion batteries (LIBs), electrodes employing thin films of active materials are preferred over their bulk counterparts due to the much improved electronic and ionic conductivity, increased specific surface area and the ease of controlling the morphology. This means that light and compact power sources with identical energy capacity to their heavier and large counterparts can be easily manufactured through thin films applications.

Thin film fabrication is not only limited to applications in LIBs. In solar cells and various electronics, for example, thin films of semiconductors and conductors are also of great importance with the aim of replacing materials that are expensive and in short supply. In this field, copper (Cu) has emerged as an ideal candidate for

applications in microelectronic devices. It is abundant, and an excellent electrical conductor with a very low electrical resistivity ($1.67\ \mu\Omega\ \text{cm}$), only second to silver, but more affordable. Additionally, Cu has excellent resistance against electro-migration, in comparison to aluminum which is currently used for interconnects in microelectronic devices [3].

Owing to the above-mentioned benefits of thin films' applications in LIBs and electrical devices, a considerable number of techniques have been established for the fabrication of these thin films. In this chapter, some of the effective techniques used in the deposition of thin films are described and discussed in Section 2.

2. Established methods for fabricating thin films

The fabrication techniques can be divided into two categories representing (1) gas phase and (2) liquid phase fabrication methods for thin films as outlined in **Table 1**. In this context, the gas phase fabrication methods are methods that involve the deposition of materials either from small particles of bulk solid materials or chemical precursors in vapor form whereas the liquid phase fabrication methods refer to the methods involving a reaction between a substrate and a chemical precursor in a liquid state.

1. Gas phase fabrication methods	2. Liquid phase fabrication methods
1. Magnetron sputtering	1. Electrospray deposition
2. Pulsed laser deposition	2. Electrochemical deposition
3. Atomic layer deposition	3. Sol-gel method
4. Chemical vapor deposition	4. Molecular precursor method

Table 1.
List of some of the methods for fabricating thin films for LIBs and devices.

2.1 Gas phase fabrication methods

2.1.1 Magnetron sputtering

This is one of the most well-established techniques that is widely used in the industries to fabricate coatings of many different materials, including metals, semiconductors, and alloys [4, 5]. Thin films fabricated *via* magnetron sputtering prove to be of superior quality in comparison to those fabricated using other gas phase methods [4, 6]. The schematic representation of the magnetron sputtering set-up is shown in **Figure 1**.

Before deposition, the chamber is evacuated to ca. 10^{-4} kPa and then refilled with Ar gas which is used as the sputter gas. Using strong electrical and magnetic field, magnetron sputtering employs the bombardment of the selected target's surface by Ar^+ ions which are formed as a result of the collision between Ar gas atoms and electrons trapped within the magnetic field. The Ar^+ ions are attracted toward the negatively charged target (cathode) and the bombardment leads to the ejection of the targets particles which are then redeposited as a thin film on the substrate placed on the anode, opposite to the target. Depending on the type of power source utilized, magnetron sputtering can be divided into two types namely, (1) direct current (dc) magnetron sputtering and (2) radio frequency (rf) sputtering. While dc magnetron sputtering is relatively cheaper in comparison to rf, only electrically conductive targets like metals or doped semiconductors are used [7]. Additionally,

Figure 1.
Schematic representation of a magnetron sputtering equipment and deposition process.

reactive gases such as oxygen or nitrogen gas are used to react with the sputtered materials, in the fabrication of thin films for metal oxides or nitrides, respectively. The technique is referred to as “reactive magnetron sputtering”. **Table 2** lists the superiorities and limitations associated with the magnetron sputtering technique.

Superiorities	Limitations
1. Well-established for the deposition of various elements, alloys, and compounds	1. Expensive, complicated and ultrahigh-vacuum systems required
2. Ability to fabricate thin films of high quality and identical composition with the target materials	2. Low deposition rates and low ionization efficiencies
	3. Expensive target materials.
	4. High substrate effect by the sputtered particles

Table 2.
Superiorities and limitations associated with the magnetron sputtering technique.

2.1.2 Pulsed laser deposition (PLD)

The schematic representation of a PLD setup is shown in **Figure 2**. The PLD technique employs the ablation of a target material with a strong, pulsed laser beam to produce a plume of vaporized materials which is then re-condensed and deposited onto a substrate, placed opposite the target, under a reduced pressure atmosphere of ca. 10^{-1} – 10^{-5} kPa [8–10]. Depending on the target material, its morphology, and the laser pulse wavelength and duration, there is a specific threshold power density that is required to cause ablation [11]. Therefore, a good understanding of the various parameters is required for a successful plume generation and subsequent thin film deposition. The stoichiometric transfer of

Figure 2.
Schematic representation of PLD setup.

materials from the target to the substrate earned PLD a reputation as fabrication of choice for thin films with complicated stoichiometry or sandwich structures [12], in comparison to other gas phase techniques.

Although the fabrication of thin films with identical stoichiometry as the target materials is one of the superior characteristics of PLD, the stoichiometry can be compromised when multi-component materials with volatile constituents are used [11–13]. As a remedy, a background gas such as oxygen or nitrogen is introduced in the reaction chamber to compensate for the lack of stoichiometry, during the fabrication of metal oxides or nitrides’ thin films, respectively. The superiorities and limitations of the PLD technique are summarized in **Table 3**.

Superiorities	Limitations
1. Stoichiometric transfer of materials from the target to the thin film	1. Expensive, complicated and ultrahigh-vacuum systems are required
2. Ideal for fabricating multi-layered thin films	2. Difficult to scale-up for mass production
3. Ideal for the deposition of thin films for high- T_c superconductors	3. Unwanted ablation impurities are often incorporated in the thin film

Table 3.
Superiorities and limitations associated with the PLD technique.

2.1.3 Atomic layer deposition (ALD)

The ALD technique is based on sequential and self-limiting reactions of a chemical precursor in vapor form, with an activated or functionalized surface of the substrate [14, 15]. The self-limiting property of this technique is realized in a sense that, if all functional sites on the substrate have reacted, no further reaction between the chemical precursor and the substrate will take place [14, 16]. **Figure 3** illustrates the concept of ALD in the fabrication of a TiO_2 thin film. The steps are defined as follows: (a) precursor exposure, (b) purge, (c) reactant exposure, and (d) purge. By repetition of step (a)–(d), layers of TiO_2 can be easily formed and the thickness can be controlled at the atomic level. Under a vacuum pressure of ca. 10 kPa or less, the chemical precursors are maintained in a vapor phase by adjusting a specific temperature referred to

Figure 3.
Schematic representation of 1 cycle of an ALD process for the deposition of a TiO₂ thin film from titanium tetrachloride and water.

as the “ALD temperature window” [17], to achieve optimum reaction kinetics and avoiding condensation or thermal decomposition of the precursor.

The superiority of ALD over other gas phase processes for the deposition of thin films is realized through its exceptional conformity, the ability to control thickness at the atomic level and tunable film composition [15, 18, 19]. Through this route, the deposition of thin films on substrates with highly-structured geometries can be easily achieved, and ALD has been considered as the ideal method for fabricating highly conformal seed layers [20, 21]. This is also of great importance for applications in the concept of integrated batteries [22], that aims at maintaining the storage capacity of miniaturized LIBs. Although the fabrication of metallic copper thin films has been achieved [17, 21, 23–25], the deposition of metallic thin films is generally limited due to the lack of precursors suitable for ALD processes. The vaporization of chemical precursors, difficulty in controlling their thermal decomposition and lack of efficient self-limited reactivity with surfaces are some of the challenging aspects in ALD [19]. In addition, during the designing stages of certain chemical precursors, the by-products associated with the proposed chemical reaction need to be carefully considered as toxic or corrosive chemicals are likely to be those by-products. **Table 4** lists the superiorities and limitations of the ALD technique.

Superiorities	Limitations
1. Suitable for the fabrication of highly conformal thin films	1. Low deposition rates
2. Chemical reactions are highly selective toward the substrates and are self-limiting	2. Requires functionalized substrates to ensure reaction with the chemical precursors
3. Thickness control at atomic scale allows for the deposition of ultra-thin films	3. The technique is limited due to the unavailability of suitable chemical precursors

Table 4.
Superiorities and limitations associated with the ALD technique.

2.1.4 Chemical vapor deposition (CVD)

Defined as the deposition of solids onto heated substrates from chemical reactions in vapor phase [26, 27], CVD represents a versatile deposition technique of thin films for a wide range of materials, under vacuumed atmospheres and temperatures over 600°C, and it is an established technique for the deposition of thin film for microelectronics, ohmic and Schottky diode contacts, diffusion barriers, wear-resistant coatings, etc. [26–29]. The schematic representation of a CVD setup is shown in **Figure 4**.

Figure 4.
Schematic representation of a CVD setup.

In a typical CVD experiment, a combination of chemical precursors showing stable vaporization behavior is carefully selected. Using an inert carrier gas, usually Ar or N₂ gas, the vaporized precursors are carried into an evacuated furnace (reaction chamber) and mixed with an additional reactive gas or two. In the fabrication of metal oxide thin films, oxygen gas is used as the additional carrier/precursor gas. On the other hand, if the desired thin film is metallic, such as Cu, a reducing atmosphere is created by using H₂ gas [30, 31].

The CVD technique benefits from the fact that it does not require ultrahigh vacuum systems like in the magnetron sputtering and PLD techniques [26, 32]. In addition, CVD is a kinetically driven process, associated with minimized agglomeration and also benefiting from faster deposition rates, in comparison to ALD [32, 33]. Because different precursors have different evaporation rates, it is generally difficult to deposit multicomponent thin films by CVD. Other drawbacks of CVD include possible chemical and safety hazards of toxic, corrosive and flammable precursors or exhaust gases, and poor thin film adhesion-strength [27, 28]. The superiorities and limitations associated with the CVD technique are summarized in (**Table 5**).

Superiorities	Limitations
1. High deposition rates	1. High temperatures are required to decompose the chemical precursors
2. High throwing power that allows for the coating of deep recesses, holes and other complicated 3-D configurations	2. Chemical precursors with high vapor pressure are often hazardous and toxic
3. Does not require ultrahigh-vacuum systems	3. The required neutralization of toxic and corrosive byproducts raises the cost of the technique

Table 5.
Superiorities and limitations associated with the CVD technique.

2.2 Liquid phase processes

2.2.1 Electrospray deposition (ESD)

ESD involves the deposition of charged particles formed as a result of liquid atomization by an electrical force. The atomization of the liquid by electrical force allows for the generation of small particles, of narrow size distribution which can be uniformly dispersed over the substrate and, ESD has been considered as a promising technique for the formation of high-quality layers and films [34]. If the ESD process is carried out at elevated temperatures, thin film formation is achieved through the thermal decomposition of the precursor solution during deposition [35] and the process is referred called “electrospray pyrolysis (ESP).” The schematic representation of the ESD setup is shown in **Figure 5**.

Figure 5.
Schematic representation of an ESD setup.

As shown in **Figure 5**, the ESD method is based on supplying a precursor solution through a metallic capillary which is maintained at high electrical potential. Ideally, the solution forms a Taylor cone at the tip of the capillary and emitted as a solution jet composed of many highly charged droplets that are homogeneously dispersed in the space between the nozzle and the counter metallic plate (substrate holder) by Coulomb repulsion forces [34]. The quality of the resultant thin films can be easily controlled by adjusting variables such as the applied voltage, distance between the atomizing nozzle and, the flow rate, concentration and amount of the precursor solution.

In addition to a very low throughput associated with the ESD technique, thin film deposition on insulating substrates is generally not possible due to charge accumulation on the substrate, which leads to the repulsion of more incoming charged particles [34]. Modifications such as the use of alternating current (ac) [36] and extractor electrodes [34] have been employed to solve the charge repulsion issue and ensure the thin film deposition on insulating substrates *via* ESD. However, this complicates an initially simple experimental setup. The superiorities and limitations of the ESD technique are listed in **Table 6**.

Superiorities	Limitations
1. Simple instrumentation	1. The strong electric field is required
2. Uniform coating on large areas and easy controlling of the surface morphology	2. Thin film fabrication on insulating substrates is challenging
3. The rate of deposition can be easily controlled by adjusting the voltage and flow rate	3. The technique is associated with low throughput
	4. The technique is very sensitive to the physical properties of the used liquid and it's very difficult to obtain a stable cone-jet throughout the experiment

Table 6.
Superiorities and limitations associated with the ESD technique.

2.2.2 Electrochemical deposition (ECD)

Considered as one of the cheapest methods for the deposition of thin films, ECD represents a major technology for mass production of large area metallic protective coatings in the industry [37]. The deposition technique employs a combination of reduction and oxidation reactions of chemical precursors in electrolytes of aqueous solutions, organic solutions or fused salts [38, 39]. In addition to cost, other advantages of the ECD include low fabrication temperature, high purity and, the ease of controlling thin film thickness, uniformity and rate of deposition by adjusting the deposition parameters [40–42]. The electrochemical technique can be divided into two groups, namely, (1) electrolysis plating which uses external power source to drive the electrochemical reaction that leads to the deposition of a thin film onto an electrically conductive substrate and, (2) electroless plating which does not require external power supply but requires the use of catalysts to activate the surface of the specimen. The schematic representations of the electrochemical techniques for the fabrication of metallic copper thin films are given in **Figure 6**.

During electrolysis deposition, the external power source causes the dissolution of the metal from the anode (usually a copper rod or plate). The dissolved Cu^{2+} ions are then reduced and redeposited on the surface of the electrically conductive substrate (Cathode). An electrolytic solution involving a salt of copper such as CuSO_4 is used for the electrochemical bath to maintain the balance of Cu^{2+} ions. In electroless plating, the electrolytic solution is also the source of the Cu^{2+} ions and a reducing agent such as formaldehyde (HCHO) is added to the plating bath. The introduction of a substrate with an activated surface (by PdCl_2 or SnCl_2) initiates the reduction of Cu^{2+} to metallic copper, subsequently forming a film on the surface of the substrate. In both the electrolytic and electroless plating, various alkaline or acidic electrolytic solutions are used and are important for maintaining the pH and stabilities of the plating baths [43].

Figure 6. Schematic representation of the electrochemical deposition techniques. (a) Electroplating. (b) Electroless plating.

Unlike in the field of metal plating, the deposition of thin films with semiconducting properties is challenging due to complications in controlling the reaction kinetics of multiple compounds in the solutions, at ppm level [37]. However, the major breakthrough came with the preparation of CdTe layers for solar cells and modules and, since then films of semiconducting materials such as CIGS [37] and LiMn_2O_4 [44] have been successfully fabricated. Although electroless plating is considered as a promising technique for the deposition of thin films especially on insulating substrates, the use of PdCl_2 or SnCl_2 compromises the quality of the thin films [45]. In addition, the selection of the chemical components for the electrolytic solution is important for ensuring that the reduction reaction occurs only on the surface of the activated substrate [43]. **Table 7** lists some of the well-known superiorities and limitations of the ECD techniques.

Superiorities	Limitations
1. Inexpensive instrumentation	1. Poor adhesion, the inclusion of cracks, blisters, and pinholes in the resultant thin films
2. Applied at room temperatures and pressures	2. Toxic supporting electrolytes or complexing agents such as cyanide are used
3. Properties of the thin films can be easily controlled by modifying the electrochemical variables	3. The substrate must be conductive. If not, a catalyst is required
4. Suitable for large area deposition	

Table 7.
Superiorities and limitations associated with the ECD technique.

2.2.3 Sol-gel method

The sol-gel method has emerged as a method of choice for the fabrication of ceramics and glasses and, it is considered as a cost-effective alternative to the well-established gas phase processes. The sol-gel method is a two-chemical processes technique based on the hydrolysis and condensation of molecular precursors and has since been considered to be capable of offering new routes for the low-temperature fabrication of oxide materials [46]. Because all gel products may contain nanoparticles or are nano-composites, the sol-gel method has been deemed as typical nanotechnology [47] and the fabrication of thin films can be easily achieved after its integration with spin-coating or dip-coating.

In a typical sol-gel process, metal precursors (of the desired metal oxide) derived from metal salts in aqueous solutions, metal alkoxides in organic solvents, or a combination of the two are used. During the hydrolysis step, metal-hydroxide groups are formed by changing the pH of the aqueous solution or adding water to the metal alkoxides. The subsequent condensation reaction results in the formation of metal-oxygen-metal bonds, with different polymerization and poly-condensation processes leading to the gradual formation of the solid phase network [48]. Although a network of metal-oxygen-metal bonds of the desired metal oxide is obtained from the polycondensation step, additional drying and annealing steps are required for the removal of organic materials and improvement of the crystallinity of the resultant thin film. A typical sol-gel process for the formation of SiO_2 from silicone alkoxides is given in **Figure 7** [49].

Although the sol-gel method has become an indispensable technique in the fabrication of thin films for metal oxides, principally, the fabrication of metallic thin films is not viable. In addition, a good understanding is required for the selection of appropriate precursors and the sophisticated chemical processes leading to the hydrolysis and condensation. The stabilization of the transition metals against hydrolysis, condensation, and other nucleophilic attacks is generally challenging. It

Figure 7.
Typical sol-gel process for SiO₂ formation from silicon alkoxides [49].

is also important to make sure that the transition metal is sufficiently saturated in solution, to avoid different reaction mechanism. Finally, proper control of the moisture and hydrolysis conditions is required to avoid precipitation of the transition metal alkoxides [48]. Therefore, all these aspects make the preparation of suitable coating precursors for the sol-gel method quite complicated. The superiorities and limitations of the sol-gel method are presented in **Table 8**.

Superiorities	Limitations
1. Inexpensive instrumentation 2. Thin films of metal oxides can be fabricated at relatively low temperatures in comparison to the conventional melting technique	1. The chemical precursors are not stable against hydrolysis and side reactions 2. High annealing temperatures are required to improve the crystallinity of the film due to the involved rearrangement of the metal-oxygen-metal network

Table 8.
Superiorities and limitations associated with the sol-gel technique.

2.2.4 Molecular precursor method (MPM)

The molecular precursor method is an effective, wet chemical process that was developed by the current authors, for fabricating nano-crystalline thin films of metals and, various metal oxides and phosphates [1, 49–53]. In the fabrication of these thin films by the MPM, metal complexes are dissolved in ethanol by combining them with appropriate alkylamines and this yields good coating solutions, with many practical advantages and are ideal for various coating procedures such as spin-coating, dip-coating, and flow-coating. Additionally, the development of aqueous precursor solutions have been successfully achieved [54, 55] and, these solutions can be easily applied for the fabrication of thin films *via* spray-coating at ambient conditions. To date, over 40 different kinds of thin films for metal oxides or phosphates have been easily fabricated by using the MPM. The procedure employed by

Figure 8.
 Procedure for fabricating a titania thin film via the MPM.

the MPM is represented by the example of fabricating the titanium dioxide thin film [1] illustrated in **Figure 8**. The procedure starts with the preparation of a coating solution by reacting an isolated Ti(IV) complex of ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) with dipropylamine in ethanol. The precursor solution, which shows stability against up to 10% water [56], is suitable for spin-coating onto a glass substrate and dried at 70°C to yield an amorphous film. In order to obtain a thin film of metal oxide spread homogeneously on the substrate after the subsequent heat-treatment, it is important that the precursor film is amorphous. Just as the case with the metal/organic polymers in the sol-gel method. The precursor film is then heat-treated at 450°C in air, to eliminate the organic components involved and a transparent thin film of titania is obtained.

In comparison to the sol-gel method, the MPM produces precursor solutions that are stable and can be stored for longer periods without being hydrolyzed. It is considered that thin films with much smaller crystallite sizes can be fabricated by the MPM due to the ease of metal oxides' nucleation. This is a result of a large number of crystallites instantly formed during the removal of organic ligands *via* the heat-treatment step of the MPM, in comparison to the rearrangement of polymer chains during the same stage in the sol-gel method [49]. Consequently, thin films of metal oxides can be easily fabricated at relatively low annealing temperatures *via* the MPM in comparison to the sol-gel method.

By following the procedure outlined in **Figure 8**, the fabrication of thin films for a novel thin-film lithium-ion battery (LIB) which can be charged by light irradiation, and thus functioning as a photovoltaic-LIB was recently achieved [57]. The device uses thin films of TiO₂ and LiCoO₂ deposited on fluorinated tin oxide (FTO) pre-coated glass substrates, as the anodic and cathodic active materials, respectively, and an electrolytic solution containing LiPF₆. In another study employing the MPM, the fabrication of the first *p*-type Cu₂O transparent thin film with properties identical to those of thin films fabricated by using gas phase processes was also achieved [58]. A dry-type solar cell utilizing this Cu₂O transparent thin film combined with a Vis-responsive anatase thin film also fabricated by the MPM could be successfully constructed and evaluated [49].

2.2.5 Highly conductive and well-adhered Cu thin film fabricated by heat treatment of a precursor film obtained by spray-coating an aqueous solution involving Cu(II) complexes

The compatibility of the MPM with the spin-coating and dip-coating techniques in the fabrication of a Cu thin film and embedding Cu in Si trenches has been described in our earlier reports [59, 60]. Very recently, our group succeeded in the fabrication of a highly conductive and well-adhered thin film of copper by heat-treatment of a precursor film obtained via spray-coating [55]. Spray-coating and other spray-on related techniques benefit from the relatively simple and inexpensive instrumentation set-up, reduced material losses [61], ability to be adjusted for large area deposition and produce thin films in a Roll-to-Roll and high throughput process in comparison to other solution-based techniques such as spin coating [62].

It is however important that a precursor solution suitable for spray-coating is developed. In our recent study, the stable and VOC-free solution was developed by mixing a Cu(II) complex of EDTA ($[\text{Cu}(\text{H}_2\text{edta})]\cdot\text{H}_2\text{O}$) and Cu(II) formate with ammonia, in water. The ratio of $[\text{Cu}(\text{H}_2\text{edta})]:\text{Cu(II) formate}$ was 1:4 and the total concentration of Cu^{2+} in the precursor solution was 0.1 mmol g^{-1} . The aqueous solution could be easily sprayed onto a quartz glass substrate pre-heated to 180°C , without forming solids that may clog the nozzle tip of the airbrush. The sprayed film denoted as **Fas-sprayed** was heat-treated at 350°C for 50 min in Ar gas (the resulting film is denoted **FHT**), followed by a post-annealing step whereby an identical-sized, clean quartz glass was placed on top and heat-treating at 400°C for 50 min also in Ar gas. The final resultant thin film is denoted as **FHP**. The XRD patterns of **Fas-sprayed**, **FHT**, and **FHP** are shown in **Figure 9**.

The XRD pattern of the as-sprayed film shows peaks assignable to the (111), (200) and (220) crystal phase of metallic copper at 43.4 , 50.5 and 74.2° , respectively (ICDD card no. 00-004-0836). The pre-heating temperature was sufficient to induce the crystallization of metallic copper. However, although the spray-coating was carried out in the air, at a substrate temperature of 180°C , the crystallized Cu^0 was not oxidized as there were no peaks assignable to the oxide species of copper observed in the XRD spectrum of **Fas-sprayed**. It is proposed that the carbon atoms derived from the EDTA ligand could effectively protect the Cu^0 against oxidation

Figure 9. XRD patterns of **Fas-sprayed**, **FHT**, and **FHP**. The peaks are denoted as follows: ◇ Cu and ■ Cu_2O .

at a preheating temperature of 180°C. After the heat-treating procedure, the XRD pattern of **FHT** shows additional peaks at 36.6° and 61.6° assignable to the (111) and (220) crystal phase of Cu₂O, respectively (ICDD card no. 01-071-3645). It is however notable that the as-sprayed film was not extensively oxidized by heat-treating at 350°C for 50 min under an Ar gas atmosphere containing about 10 ppm of air as an impurity. The Cu₂O phase was successfully removed during the post-annealing procedure whereby the carbon atoms remaining within the film were used to reduce the Cu⁺ to Cu⁰. As a result, the XRD pattern of the **FHP** film shows only peaks assignable to metallic copper.

Figure 10 shows the Auger Electron Spectroscopy (AES) measurements of **FHP**. The surface scan (**Figure 10a**) indicated that the thin film is composed of C and Cu, as has been confirmed by one peak at 265 eV assignable to electrons of carbon atom and three peaks (LVV) at 764, 835, and 914 eV assignable to electrons of Cu, respectively. The curve-fitting result (**Figure 10b**) revealed that all carbon atom present in the thin film is neutral. The effectiveness of the carbon atoms present in the film has been illustrated in the protection of the **FHT** film against excessive oxidation. Specifically, the ratio of Cu₂O:Cu peaks assignable to the (111) plane of each phase in **FHT** was 4:96. This implies that the carbon atoms derived from the EDTA ligand and formic acid [of Cu(II) formate] were vital for further protection of the formed Cu⁰ phase in an Ar gas atmosphere containing less than 2 ppm of oxygen gas. On the basis of our previous procedures, the post-annealing procedure accounts for the removal of up to 50% of the carbon atoms present in the film, right after the heat-treatment procedure. Therefore, it is acceptable that the neutral carbon is existing in the resultant thin film, **FHP**. Interestingly, the carbon atoms did not disrupt the electrical conductivity of the film.

Figure 11 shows the FE-SEM (a) and AFM (b) images of **FHP**. The images show morphologies composed of well-connected Cu grains and a densely deposited matrix of Cu grains can be observed from the FE-SE cross-sectional image, consequently promoting electrical conductivity within the film. The crack-free and densified film **FHP** of 100 nm thickness has an electrical resistivity of $3.8(6) \times 10^{-5} \Omega \text{ cm}$.

Figure 10.
 (a) Auger spectrum of **FHP**. Peaks are denoted as follows: ◇ Cu and ▼ C. (b) Curve-fitting results for the carbon state in **FHP**. The solid, dotted, and dashed lines represent **FHP**, C (neutral) and C (tetravalent), respectively.

Figure 11. (a) FE-SEM images showing the top and cross-section views of the **FHP** film. (b) 3D AFM image of the **FHP** film.

Figure 12. Reflectance spectra of **FHP**.

Figure 12 shows the reflectance spectra of the **FHP** film. The reflectance of **FHP** approaches over 90% in the far infrared region which is comparable to the conductive and semi-transparent Cu thin film previously reported by our group [59] and can also be useful as an excellent reflector in the far-infrared region. Results of the stud-pull coating adhesion test indicated that the thin film strongly adhered onto the quartz glass substrate with an adhesion strength of up to 37 MPa. This adhesion strength was efficiently attained without any chemical or physical modification of the substrate's surface and it is expected to be a result of the interface having bonds between Cu and the O^{2-} belonging to the quartz glass substrate.

The research for the next generations is looking at the utilization of environmentally friendly reagents to achieve the fabrication of functional thin films for

various materials. Therefore, the aqueous precursor solution used in our recent study has the potential as a promising technique for the fabrication of metallic Cu thin films for various applications. In our study, solutions involving different Cu(II) complexes were investigated. For example, a nonconductive film of copper was obtained after heat-treating a film from a solution involving the Cu(II) complex only. In addition, it is important to point out that the precursor solution with a [Cu(H₂edta)]:Cu(II) formate ratio of 1:4 gave the best results with good reproducibility. The importance of designing and mixing different Cu(II) complexes involved in the coating solution was clearly illustrated. By varying the ratio of the Cu(II) complexes in the coating solution, films with different crystal structures, morphologies, and electrical properties could be obtained. And this is the advantage of the MPM which enables to design metal complexes in coating solutions, at the molecular level. By using the spray-coating technique, our group also managed to fabricate a thin film of LCO on a non-crystalline quartz glass substrate.

Established just over 22 years ago, the MPM is a relatively new method in comparison to other thin film fabrication methods described earlier in this chapter. However, it is emerging as an effective chemical method for the fabrication of various transparent thin films of metal oxides and highly conductive thin films of metallic Cu. The superiorities and limitations of the MPM are given in **Table 9**.

Superiorities	Limitations
1. Stable and homogeneous precursors of different kinds of metal complexes can be easily prepared	1. Thermal decomposition and removal of the organic components from the precursor films are necessary
2. The coating solutions can be tailored for different coating techniques	
3. The fabrication of metal oxide thin films can be achieved at lower annealing temperatures as compared to other liquid phase processes such as the sol-gel method	

Table 9.
Superiorities and limitations associated with the MPM technique.

3. Conclusions

Various fabrication techniques for thin films applicable to energy materials and devices have been described and discussed in details. Gas phase processes such as magnetron sputtering and PLD have been identified to be capable of fabricating thin films of high quality and are well-established in the coating industry. However, expensive and complicated instruments are required. The ALD and CVD techniques are suitable for the fabrication of thin films onto substrates with complicated 3-D structures. However, potentially toxic and corrosive chemical precursors are used. Additionally, the fabrication of thin film with different chemical components is challenging due to the different properties of chemical species in the vapor phase.

The liquid phase processes are cost-effective alternatives to their gas phase counterparts. The ESD benefits from the ability to control the surface morphology of the deposited thin film but suffers from low throughput and difficulties to deposit films onto insulating substrates. ECD is well-established for the fabrication of thin films for metallic coatings such as copper, on a large area. However, the resultant thin films suffer from weak adhesion and poor surface morphology. The sol-gel method has been extensively developed for the fabrication of thin films for metal oxides at relatively low-costs in comparison to the gas phase processes. The poor stability of

the chemical precursors against hydrolysis and deviating reaction mechanisms are some of the challenges encountered.

The MPM is an emerging liquid phase process capable of fabricating thin films of metal oxides such as TiO_2 , LiCoO_2 , and *p*-type Cu_2O etc. and the functionalities of these thin films in energy devices have been evaluated in a PV-LIB [53] and a dry-type solar cell [49]. Thin films of metallic copper have also been successfully fabricated by the MPM. This shows that the MPM is earning its place among affordable and effective techniques for the fabrication of thin films for future energy materials and devices.

Although there are other additional fabrication techniques, the chapter provided an insight into some of the well-established and promising techniques for the fabrication of future energy materials and devices, taking into consideration the costs in terms of the required instrumentation and thin film deposition conditions.

Conflict of interest

The authors declare no conflict of interest.

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