

A Study of Established Methods of Thin Films for Fabrication with Energy Materials

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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.

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.

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

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

3. GAS PHASE FABRICATION METHODS

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, 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.

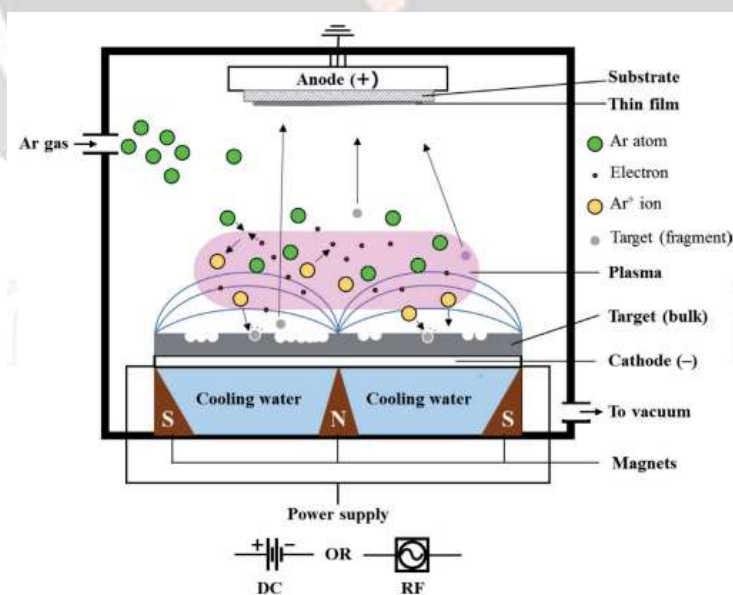


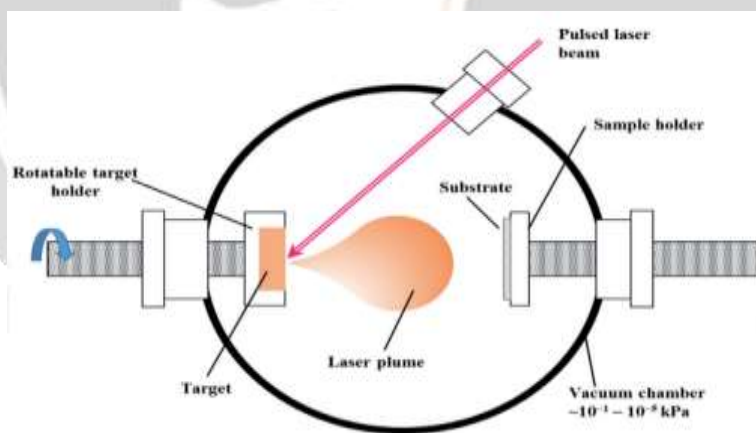
Figure 1. Schematic representation of a magnetron sputtering equipment and deposition process

Table 2. 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

2. Pulsed laser depositions (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 recondensed 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 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.

**Figure 2. Schematic representation of PLD setup****Table 3. Superiorities and limitations associated with the PLD technique**

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

3. Atomic layer depositions (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. Figure 3 illustrates the concept of ALD in the fabrication of a TiO₂ 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 TiO₂ 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 as the “ALD temperature window”, 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. 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. This is also of great importance for applications in the concept of integrated batteries that aims at maintaining the storage capacity of miniaturized LIBs. Although the fabrication of metallic copper thin films has been achieved, 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. 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.

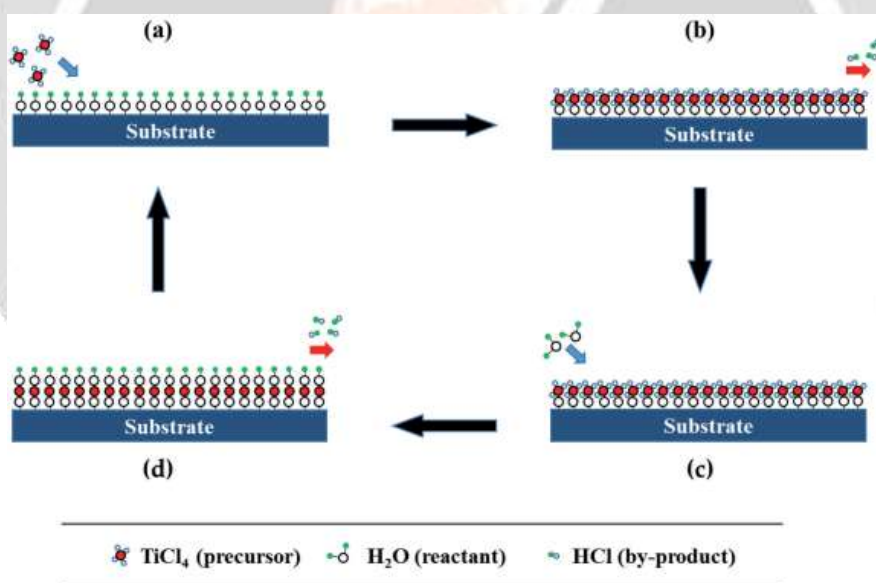


Figure 3. Schematic representation of 1 cycle of an ALD process for the deposition of a TiO₂ thin film from titanium tetrachloride and water

Table 4. Superiorities and limitations associated with 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

4. Chemical vapor depositions (CVD)

Defined as the deposition of solids onto heated substrates from chemical reactions in vapor phase, 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. The schematic representation of a CVD setup is shown in Figure 4.

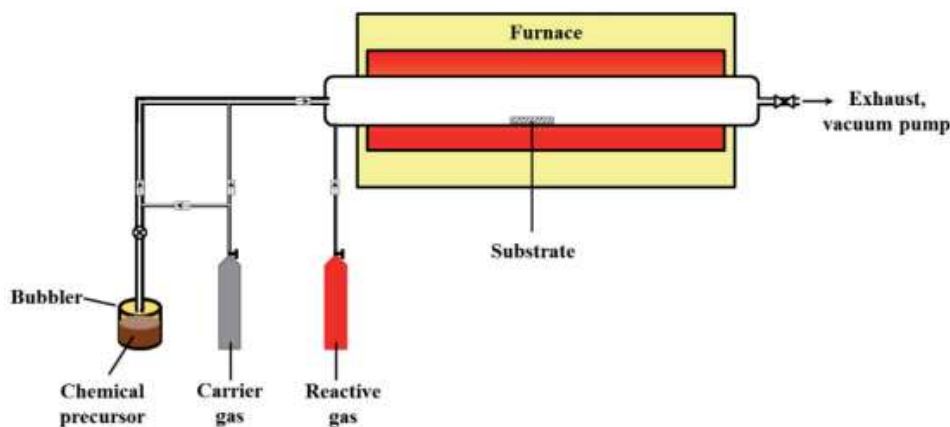


Figure 4. Schematic representation of a CVD setup

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. The CVD technique benefits from the fact that it does not require ultrahigh vacuum systems like in the magnetron sputtering and PLD techniques. In addition, CVD is a kinetically driven process, associated with minimized agglomeration and also benefiting from faster deposition rates, in comparison to ALD. 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. The superiorities and limitations associated with the CVD technique are summarized in (Table 5).

Table 5. Superiorities and limitations associated with the CVD technique

Superiorities	Limitations
<ol style="list-style-type: none"> 1. High deposition rates 2. High throwing power that allows for the coating of deep recesses, holes and other complicated 3-D configurations 3. Does not require ultrahigh-vacuum systems 	<ol style="list-style-type: none"> 1. High temperatures are required to decompose the chemical precursors 2. Chemical precursors with high vapor pressure are often hazardous and toxic 3. The required neutralization of toxic and corrosive byproducts raises the cost of the technique

4. CONCLUSION

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 TiO₂, LiCoO₂, and p-type Cu₂O etc. and the functionalities of these thin films in energy devices have been evaluated in a PV-LIB and a dry-type solar cell. 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.

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