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A brief review of atomic layer deposition: from fundamentals to applications

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Atomic layer deposition (ALD) is a vapor phase technique capable of producing thin films of a variety of materials. Based on sequential, self-limiting reactions, ALD offers exceptional conformality on high-aspect ratio structures, thickness control at the Angstrom level, and tunable film composition. With these advantages, ALD has emerged as a powerful tool for many industrial and research applications. In this review, we provide a brief introduction to ALD and highlight select applications, including $Cu(In,Ga)Se_2$ solar cell devices, high-k transistors, and solid oxide fuel cells. These examples are chosen to illustrate the variety of technologies that are impacted by ALD, the range of materials that ALD can deposit – from metal oxides such as $Zn_{1-x}Sn_xO_y$, ZrO_2, Y_2O_3, to noble metals such as Pt – and the way in which the unique features of ALD can enable new levels of performance and deeper fundamental understanding to be achieved.

Introduction

Atomic layer deposition (ALD) is a technique capable of depositing a variety of thin film materials from the vapor phase. ALD has shown great promise in emerging semiconductor and energy conversion technologies. This review is intended to introduce the reader to the basics of ALD and highlight current applications pertaining to microelectronics and energy that were selected because of their importance in either industry or research. For a more comprehensive summary of ALD and its many applications, the reader is referred to existing reviews on the topic [1–10].

As device requirements push toward smaller and more spatially demanding structures, ALD has demonstrated potential advantages over alternative deposition methods, such as chemical vapor deposition (CVD) and various physical vapor deposition (PVD) techniques, due to its conformality and control over materials thickness and composition. These desirable characteristics originate from the cyclic, self-saturating nature of ALD processes.

ALD was popularly introduced as atomic layer epitaxy (ALE) by Suntola and Antson in 1977, depositing ZnS for flat panel displays [11]. As further ALE processes were developed to incorporate metals and metal oxides, many materials were deposited non-epitaxially and the more general name of ALD was adopted to reflect this [1]. It should be noted, too, that many ALD procedures were developed from a variety of CVD processes. In contrast to their CVD analogs, the ALD procedures feature alternating exposure of chemical precursors to react to form the desired material, often at significantly lower temperatures [12].

A general ALD process is illustrated in Fig. 1. It consists of sequential alternating pulses of gaseous chemical precursors that react with the substrate. These individual gas-surface reactions are called 'half-reactions' and appropriately make up only part of the materials synthesis. During each half-reaction, the precursor is pulsed into a chamber under vacuum (<1 Torr) for a designated amount of time to allow the precursor to fully react with the substrate surface through a self-limiting process that leaves no more than one monolayer at the surface. Subsequently, the chamber is purged with an inert carrier gas (typically N_2 or Ar) to remove any unreacted precursor or reaction by-products. This is then followed by the counter-reactant precursor pulse and purge, creating up to one layer of the desired material. This process is then cycled until the appropriate film thickness is achieved. Typically,

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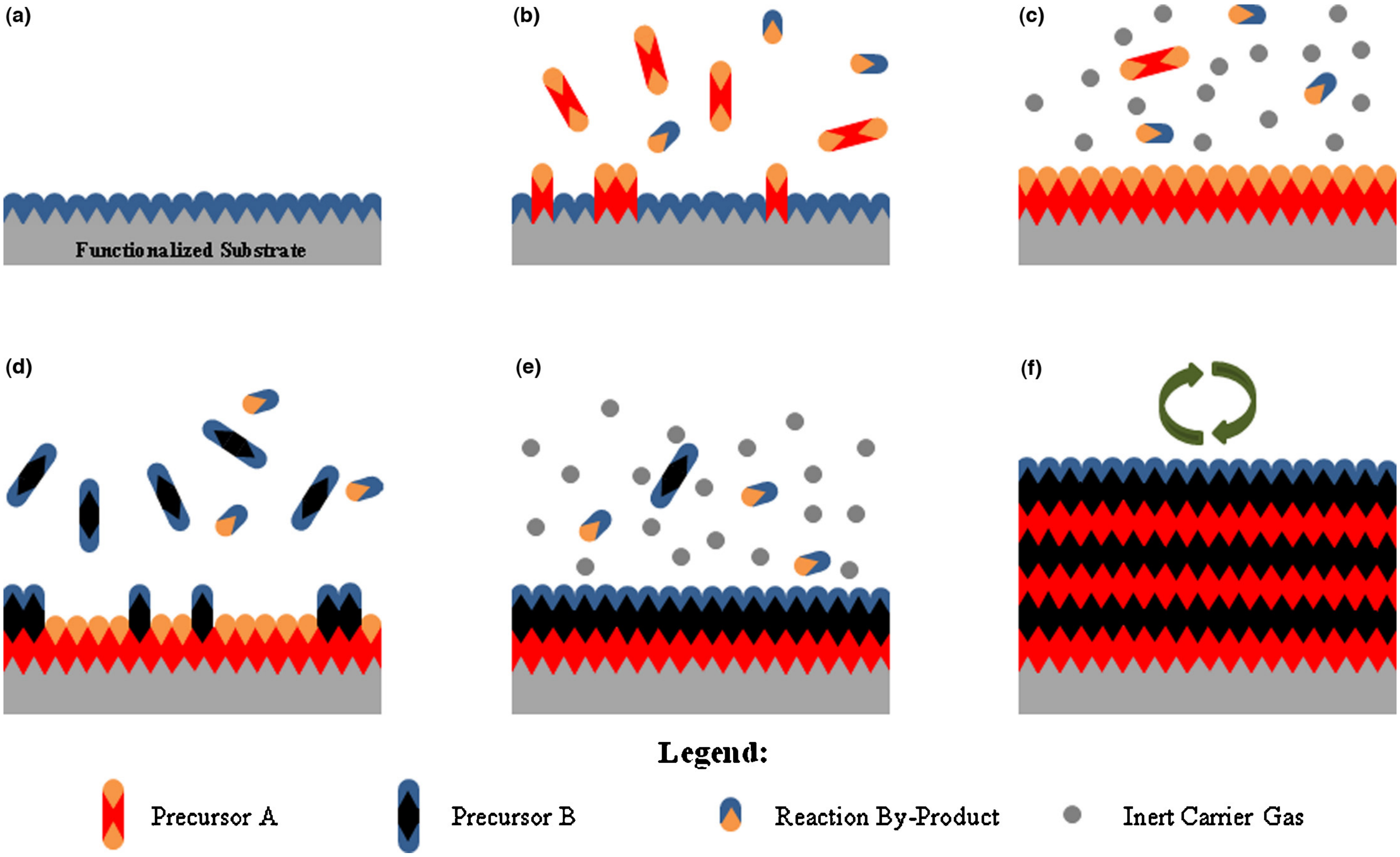

FIGURE 1

Schematic of ALD process. (a) Substrate surface has natural functionalization or is treated to functionalize the surface. (b) Precursor A is pulsed and reacts with surface. (c) Excess precursor and reaction by-products are purged with inert carrier gas. (d) Precursor B is pulsed and reacts with surface. (e) Excess precursor and reaction by-products are purged with inert carrier gas. (f) Steps 2–5 are repeated until the desired material thickness is achieved.

ALD processes are conducted at modest temperatures (<350 °C). The temperature range where the growth is saturated depends on the specific ALD process and is referred to as the 'ALD temperature window'. Temperatures outside of the window generally result in poor growth rates and non-ALD type deposition due to effects such as slow reaction kinetics or precursor condensation (at low temperature) and thermal decomposition or rapid desorption of the precursor (at high temperature). In order to benefit from the many advantages of ALD, it is desirable to operate within the designated ALD window for each deposition process.

The primary advantages of ALD are all derived from the sequential, self-saturating, gas-surface reaction control of the deposition process. Firstly, the conformality of ALD-deposited films is often the critical factor in choosing ALD over competing deposition techniques such as CVD or sputtering. Conformality of high aspect ratio and three dimensionally-structured materials is made possible by its self-limiting characteristic, which restricts the reaction at the surface to no more than one layer of precursor. With sufficient precursor pulse times, the precursor can disperse into deep trenches, allowing for complete reaction with the entire surface. Subsequent cycles allow for uniform growth on high aspect ratio structures, whereas CVD and PVD may suffer from non-uniformity due to faster surface reactions and shadowing effects, respectively. Examples of the superior conformality of ALD films are shown in Fig. 2a and b for SnS_x films on Au nanoparticles and $Ge_2Sb_2Te_5$ films over SiO_2 trenches; the ability of the process to evenly coat the substrate morphology is evident. A second apparent advantage of ALD is the thickness control of the deposited thin films. By utilizing layer-by-layer deposition, the thickness of a film can be tailored by the number of ALD cycles. Growth per cycle for many ALD films has been summarized in previous reviews [1,2] and is typically less than one Å/cycle, depending on the individual process. Another prominent advantage of ALD is composition control. Composition control has been demonstrated with materials such as zinc tin oxide (ZTO) [13] and $SrTiO_3$ [14], among many others [15–17]. These films can be deposited and compositionally controlled by tailoring ALD 'super cycles', which are composed of multiple ALD processes. For example, in ZTO deposition, adjusting the super cycle ratios for SnO_x and ZnO can tailor different conduction behavior and optical properties of the film [13]. In depositing $SrTiO_3$, ALD processes for TiO_2 and $SrCO_3$ are alternated in a super cycle at a 1:1 ratio, producing a stoichiometric $SrTiO_3$ film after annealing (Fig. 2) [14]. However, it should be noted that a nonlinear relationship between the cycle ratio and the film's atomic ratio is common for the ternary oxide processes [16,17], making it less straightforward to deposit a film with a certain desired composition. For example, additional studies on $SrTiO_3$, ALD have indicated that a 1:1 Sr:Ti atomic ratio in films is also possible for ALD cycle ratios between 0.67 and 0.82 [15]. Other complications in composition control for ternary and quaternary metal oxide ALD arise from the need for the growth windows of individual ALD processes to be thermally compatible and the way