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Perspective

Material manufacturing from atomic layer

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Abstract

Atomic scale engineering of materials and interfaces has become increasingly important in material manufacturing. Atomic layer deposition (ALD) is a technology that can offer many unique properties to achieve atomic-scale material manufacturing controllability. Herein, we discuss this ALD technology for its applications, attributes, technology status and challenges. We envision that the ALD technology will continue making significant contributions to various industries and technologies in the coming years.

Keywords: atomic-scale manufacturing, atomic layer deposition, area selective deposition, applications

In material manufacturing, while the first quarter of the 21st century is, in retrospect, a blossom of nanoscale manufacturing, the next quarter of the century will surely be the era of atomic-scale manufacturing. A clearly perceivable trend in the research community over the last several years is the fast-growing emphasis on atomic-scale engineering for materials and interfaces. For instance, in the electronics area, two-dimensional (2D) materials with the layer thickness of only several atoms have triggered tremendous research interests, as these materials have been considered the ideal lifeboat to further extend Moore's law following the 'More Moore' route [1, 2]. In the chemical catalysis area, single-atom catalysis has sparked significant interest recently, as the local atomic-scale environment tailoring offers enormous potential for the catalyst design to achieve diverse thermo-, electro-, and photochemical catalysis functionalities [3]. On the other hand, as the size of the materials for engineering shrinks down to the nanometer scale, their surfaces and interfaces, usually of only several atomic layers, become critical in determining the overall material properties. Defects located at the surfaces and interfaces are usually the notorious killer of charge transport and photoemission in optoelectronic devices, and therefore, these surface/interface defects should be carefully addressed and possibly passivated by certain atomic-scale manufacturing approach.

All these growing needs in atomic-scale material and interface engineering have prompted a highly demanding call for material manufacturing technology that can controllably handle the process precisely at the atomic-layer level for diverse sophisticated-structured materials. Atomic layer deposition (ALD) is one of the most effective manufacturing approaches in this regard. ALD utilizes well-defined surface chemistry reactions and grows materials one atomic layer at a time. Therefore, the ALD approach is atomic-scale controllable and thus can offer numerous desired properties for atomic-scale material manufacturing.

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Attributes and applications of ALD have been extensively reviewed in a number of publications [4–8], including a few published in this special issue; however, gaps and challenges for this technology are still prominent. To this end, we, in this perspective, intend to answer the following three key questions for ALD technology.

1. Why do we need atomic layer deposition?

Over the past decades, the most influential booster of ALD technology has been the integrated circuits (IC) industry. Driven by the Moore's law, there has been a huge demand to make electronic devices smaller and denser. Now in the high-end IC, many layers are only several nanometers thick and required to be deposited conformally with angstrom-level uniformity. These layers can only be made by ALD [7]. As the IC devices become more complex and three-dimensional, ALD will surely continue to be a crucial player in IC technology. Another important application area for ALD is solar cells. Commercial crystalline Si photovoltaics with passivated emitter and rear cell or tunnel oxide passivated contact structures have both adopted ultrathin ALD Al_2O_3 layers for passivation [9, 10]. As for next-generation sensing devices (e.g. CMOS image sensors [11], gas sensors [12], and chemical sensors [13]) and energy conversion and storage devices (e.g. perovskite solar cells [14], batteries [15, 16], fuel cells [17], and electrolyzers for H_2 production [18] and CO_2 reduction [19]), ALD technology has also been demonstrated to be important. For example, ALD empowers researchers to accurately design and fabricate various high-performance components for Li-ion batteries [20]. It enables precise deposition of ultrathin coating films on the cathode and anode materials [21], and these coating films can be tailored to modify the properties of the materials, enhancing their performance and stability within the battery system [22, 23]. In addition, ALD has also shown great potential in biomedicine applications, such as drug delivery, tissue engineering, biosensors, and bioelectronics [24, 25]. Certainly, we cannot list all the applications of ALD; and with the dynamic advancement of the ALD technology, many new applications are continuously emerging.

2. How can we achieve atomic layer deposition?

Briefly speaking, a typical ALD process is executed in a cyclic manner, where each ALD cycle consists of two or more gas-solid surface chemical reactions performed sequentially. By carefully engineering the precursor molecular structure and deposition conditions [26], self-limited atomic-layer growth of material can be realized in each ALD cycle. This self-limited growth behavior is in stark contrast to a conventional CVD process, where the precursors are continuously and simultaneously supplied so that the film growth is not self-limited. Therefore, in ALD, the thickness of the deposited films can be digitally controlled to realize the atomic level precision (ca. 1 Å). Moreover, the composition of the deposited films can, in theory, be tuned also at the atomic level. However, the above attributes rely on the assumption that all involved surface reaction processes are ideal. Unfortunately, this assumption is almost never met—non-ideal factors always exist to some extent. For instance, the ALD byproduct may not be sufficiently volatile to liberate from the surface, which could block the reactive sites and therefore reduce the per-cycle film growth [27]; the ALD precursor molecule may partly decompose on the surface, which could lead to impurities in the films [28]. To tackles these issues, one may need to carefully choose the precursor types and deposition conditions, such as temperature, pressure, and perhaps using plasma assisting [26]. With optimized deposition conditions, high-quality heteroepitaxial thin films can also be grown by ALD [29].

Besides the layer-by-layer growth, area selective deposition (ASD) in atomic layer has some killer applications in transistor downscaling. Selective ALD allows controlled growth in specific regions while leaving adjacent areas intact. Over time, various template-assisted selective ALD methods and inherently selective ALD strategies have been developed [30]. The template-assisted process relies on inhibitors such as self-assembled monolayers. By introducing molecules, the adsorption of ALD precursors can be blocked, preventing deposition on passivated areas. To further advance downscaling, inherently selective ALD techniques have been developed, which include modifying defects and selectively growing on desired heterogeneity regions like terraces, step edges, and facets of the same or different materials [31]. The inherent selectivity originates from thermodynamic differences, and tuning kinetic parameters such as temperature and partial pressure could expand the selective process window. More ASD approaches are expected to emerge, providing further advancements for the semiconductor industry. These approaches heavily rely on nucleation control, which is closely related to surface reactions. By tuning the substrate's electronegativity, alkalinity, or acidity, the selectivity can be enhanced. Nevertheless, some challenges remain to be addressed. For instance, during ALD on defined nanopatterns, lateral growth often occurs, resulting in a 'mushroom'-like structure. To minimize the lateral expansion, orthogonal growth is being pursued. Additionally, defects in non-growth areas need to continual elimination during deposition. Incorporating multiple ALD cycles with selective etching or correction steps appears promising for cleaning or renewing the non-growth surface.

3. What are the status quo and challenges?

With the great efforts from the ALD community, there have been hundreds of ALD processes reported so far [32]. Although some materials are still missing, the capability of ALD has already covered a large portion of materials. However, when it comes to a specific application, more consideration is needed, particularly on process compatibility. For instance, in the emerging area of amorphous oxide semiconductor (AOS) thin film transistors, the ALD Al_2O_3 gate-dielectric should be deposited from trimethylaluminum and O_3 [33], rather than using water as the oxygen source, because the latter is detrimental to the underneath AOS channel materials. Therefore, the compatibility issue should always be cautioned when adopting a reported ALD process for a new application.

Throughput is also a concern for large-scale ALD processing. Although wafer-scale processing is mature in the IC industry, several emerging applications, such as displays and solar cells, need to deposit ALD films on several m^2 large-area substrates and/or with extremely high throughput. To this end, batch ALD or spatial ALD may be a solution [34]. However, both batch and spatial ALD are more sensitive to surface reaction kinetics and gas-phase mass transport. Therefore, a good understanding of surface chemistry is highly important for large-scale manufacturing. As for the scalable manufacturing equipment, it is also vital to have optimal reactor designs that ensure uniform film deposition across large-area substrates. Quantitative optimizations of process parameters, such as precursor delivery and purge times, precursor partial pressure, are necessary to increase the production rate and decrease the cost. Additionally, incorporating *in-situ* or *ex-situ* metrology techniques can provide valuable insights into film thickness, composition, and quality throughout the deposition process. Advanced control systems that enable real-time monitoring and feedback control of critical process parameters, including temperature, pressure, precursor pulse, and exposure time, are crucial for achieving consistent film quality and reproducibility. Overcoming these challenges requires dedicated efforts and innovative approaches from engineers and researchers in various fields.

In summary, ALD technology has the potential to revolutionize material manufacturing by offering atomic-scale controllability and precision on thickness and composition, resulting in materials and structures with unique and desirable

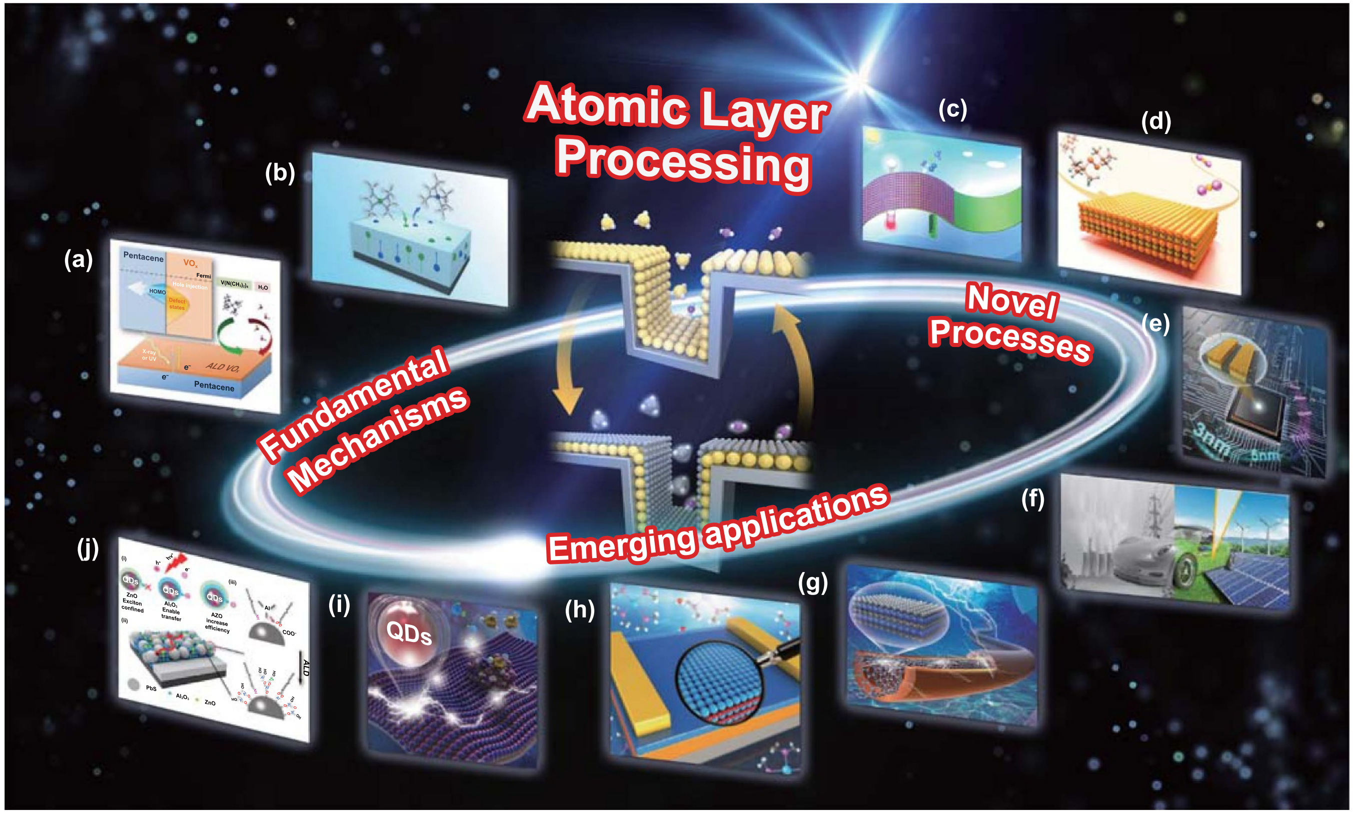

Figure 1. Summary of the representative research and application areas of the ALD technology. (a), (b) Fundamental mechanism investigations, (c)–(e) novel process development, and (f)–(j) application explorations. (a) [35], (b) [36], (c) [6], (d) [37], (f) [38], (g) [39], (h) [40], (i) [41], (j) [42]. Reprinted with permission from [35]. Copyright (2017) American Chemical Society. Reprinted with permission from [36]. Copyright (2021) American Chemical Society. Reproduced from [6] with permission from the Royal Society of Chemistry. Reprinted with permission from [37]. Copyright (2020) American Chemical Society. Reproduced from [38]. © The Author(s). Published by IOP Publishing Ltd CC BY 4.0. Reproduced from [39] with permission from the Royal Society of Chemistry. [40] John Wiley & Sons. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim Reproduced from [41]. CC BY 4.0. Reprinted with permission from [42]. Copyright (2020) American Chemical Society.

properties. The perspectives for ALD technology are promising (figure 1), and ongoing research is exploring new applications, improving the efficiency and throughput of the processes, and discovering new materials and structures. As a result, ALD technology is poised to continue making significant contributions to various industries and technologies in the coming years.

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