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Recent Advances and Development in Atomic Layer Deposition

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Abstract:-
This research paper examines progress made in Atomic Layer Deposition (ALD), both for computational and experimental methodologies, and provides an outlook of this emerging technology in comparison with other film deposition methods. This paper discusses experimental approaches and factors that affect the deposition and presents simulation methods, such as molecular dynamics and computational fluid dynamics, which help determine and predict effective ways to optimize ALD processes, hence enabling the reduction in cost, energy waste and adverse environmental impacts. Specific examples are chosen to illustrate the progress in ALD processes and applications that showed a considerable impact on other technologies.

Keywords:- atomic layer deposition, molecular dynamics, computational, thin film etc.

1. Introduction:-
During atomic layer deposition a film is grown on a substrate by exposing its surface to alternate gaseous species (typically referred to as precursors or reactants). In contrast to chemical vapour deposition, the precursors are never present simultaneously in the reactor, but they are inserted as a series of sequential, non-overlapping pulses. In each of these pulses the precursor molecules react with the surface in a self-limiting way, so that the reaction terminates once all the reactive sites on the surface are consumed. Consequently, the maximum amount of material deposited on the surface after a single exposure to all of the precursors (a so-called ALD cycle) is determined by the nature of the precursor-surface interaction. By varying the number of cycles it is possible to grow materials uniformly and with high precision on arbitrarily complex and large substrates.
ALD is considered one deposition method with great potential for producing very thin, conformal films with control of the thickness and composition of the films possible at the atomic level. A major driving force for the recent interest is the prospective seen for ALD in scaling down microelectronic devices according to Moore's law. ALD is an active field of research, with hundreds of different processes published in the scientific literature, though some of them exhibit behaviours that depart from that of an ideal ALD process. Currently there are several comprehensive review papers that give a summary of the published ALD processes, including the work of Puurunen, Miikkulainen et al., Knoops et al., and Mackus & Schneider et al. An interactive, community driven database of ALD processes is also available online which generates an up-to-date overview in the form of an annotated periodic table.
The sister technique of atomic layer deposition, molecular layer deposition (MLD), is employed when organic precursors are wished to be used. By combining the ALD techniques, it is possible to make highly conformal and pure hybrid films for many applications.

1.1 Definition of ALD :- Atomic layer deposition (ALD) is a thin-film deposition technique based on the sequential use of a gas-phase chemical process; it is a subclass of chemical vapour deposition. The majority of ALD reactions use two chemicals called precursors (also called "reactants"). These precursors react with the surface of a material one at a time in a sequential, self-limiting, manner. A thin film is slowly deposited through repeated exposure to separate precursors. ALD is a key process in fabricating semiconductor devices, and part of the set of tools for synthesising nanomaterials.

1.2 Background approach of the Study:-

The concept of ALD was first introduced by Prof. V.B. Aleskovskii in his Ph.D work in 1952. The work was consolidated in another work on the process together with Prof. Kolt'sov in 1960, with which they published the principles of ALD with the title of 'Molecular Layering' .

In 1970, Dr. Tuomo Suntola along with other researchers developed an industrial thin film deposition technology and called it 'atomic layer epitaxy' (ALE). This technology found its first application in thin-film electroluminescent (TFEL) flat panel display, and the technology and materials selection has grown over years and find applications in photo voltaics, catalysis, semiconductor devices and many others.

ALD occurs by chemical reactions of two or more precursors injected alternately into a chamber where a substrate is placed at a given temperature and pressure to enable materials deposition on the substrate's surface layer by layer. Unlike chemical vapour deposition (CVD) and other similar deposition methods, in ALD the precursors are not pumped simultaneously, they are pulsed sequentially. Although there are similarities between ALD and CVD, the distinction lies in the self-limiting characteristics for precursor adsorption, alternate and sequential introduction of the precursors and reactants.

1.3 Advantages and Disadvantages of ALD

The outstanding feature of ALD in comparison to other deposition techniques such as CVD and PVD is the self-limiting chemisorption of precursors in each half-cycle. This makes ALD unique in sub-nanometre film thickness and conformality control, offering next to (nearly) equal growth-per-cycle values for identical precursors in different equipment. The main advantages and disadvantages of the ALD process. ALD can create high-quality film with conformality and most importantly it works at low temperatures. ALD is exceptionally effective at coating surfaces that exhibit ultra-high aspect ratio topographies, as well as surfaces requiring multilayer films with good quality interfaces. However, ALD is facing some challenges. The ALD process is a high precision process and this often leads to high precursor gas usage and energy. Approximately 60% precursor dosage is wasted in the ALD process which implies that most of the energy has been wasted as well as the concomitant labour. This low material utilization efficiency is shown to be about 50.4% of TMA deposited on wafers as revealed by experiments. For instance, in the Al2O3ALD process, ~4.09 MJ energy is consumed for the deposition of a film with 30 nm thickness and this shows the energy-intensive nature of the ALD process and invariable energy wastage. In a previous study on nano-particle emissions, Al2O3 ALD process shows that the total nano-particle emissions with the diameter of less than 100 nm are in the range of 6.0 × 105 and 2.5 × 106 particles in 25 cycles of Al2O3 ALD process. Another drawback in ALD for commercial use is the cost-effectiveness which is principally due to its deposition rate; however, this challenge has been partially overcome using spatial atmospheric ALD.

1.4 Methods for studying ALD

Research study on ALD process was categorized into two main categories : numerical and experimental. In the experimental studies, researchers have improved the deposition of the films by adjusting the conditions such as; pressure, temperature, purge time, concentration, etc. The ALD process has quite extensive materials range to choose from however not all materials can be used; hence, the need for simulation to determine and predict which effective reaction pathways are necessary. Some important methods discussed below.

1.4.1 Numerical Methods :

1.4.1.1 **Monte Carlo** 3D (three-dimensional) Monte Carlo model was used by Cremers et al. to compare the deposition of an infinite array of holes and infinite arrays of pillars using atomic layer deposition on large 3D surface area. They observed that the required exposure to conformally coat an array of holes is determined by the height to width ratio of the individual holes and is independent of their spacing in the array. In studying the conformality of plasma enhanced ALD (PEALD) using the Monte Carlo method, Knoops et al. used the recombination probability, the reaction probability and the diffusion rate of particles to observe the conformal deposition in high aspect ratio structures (step coverage). They identified three deposition positions: a reaction limited regime, a diffusion limited regime and a recombination limited regime. From their findings, conformal deposition can be achieved in high aspect ratio structures with a low value of recombination probability. Shirazi and Elliott studied the atomistic kinetics of atomic layer deposition using the Monte Carlo method derived from density functional theory (DFT). They looked at the early stage adsorption of the ALD precursor, the surface proton kinetics, the steric effects, influence of remaining fragments on adsorption sites, densification of the precursor, migration, and cooperation of the precursors. They concluded that the essential chemistry of the ALD reactions depends on the local environment at the surface.

1.4.1.2. Molecular Dynamics

Molecular dynamics (MD) is a numerical method that uses Newton's equations of motion for computationally simulating the movements of atoms and molecules. The techniques depend on the description of the interaction of molecules-force field and are extensively used in chemistry, physics, biophysics and biochemistry. MD more often is about developing quantitative predictions of molecular shape, sizes, flexibilities, the interactions with other molecules, its behaviour under pressure, and the relative frequency of one state or conformation compared to the others. Using Newton's equation of motions, the simulation calculates the forces between the atoms at each time step and updates the positions of the atoms at the following time step. High costs and difficult chemical management associated with ALD studies have made more researchers to conduct numerical modelling of the ALD process to understand and study the operation process. In modelling, further insight into the ALD process is gained, hence minimizing the precursors' inputs and wastes and also reduces the potential environmental impacts in future industrial productions.

As compared to other modelling methods, there are few studies using molecular dynamics for ALD modelling. In MD simulations the non-bonded interactions between atoms that are being considered and calculated using the Lennard-Jones potential parameters and the columbic potentials.

1.5 Experimental Methods :-

ALD grown materials which include oxides, nitrides, sulfides, pure elements and inorganic compounds are realized through the pulse/purge process in ALD reactors. The ALD film deposition methods experimentally depend on the factors such as the nature of the substrate, the deposited materials and the reactor design. The growth rate in ALD is strongly dependent on the aspect ratio of the substrate and the reactor design. Increase in the surface area and volume of an ALD reactor leads to an increase in pulsing and purging time. Substrate structures with high aspect ratio require longer pulsing and purging time for the gases to disperse evenly into the trenches and the three-dimensional features. Spatial ALD was introduced to overcome the longer pulsing and purging time by replacing the pulse/purge chambers spatially revolving heads. This exposes the substrate to a specific gas precursor-based location within the reactor. Numerous reactants/precursors are used in ALD. Non-metal and metal precursors react differently and show different features so are organic compounds.

1.5.1 Reactor Conventional ALD reactors, such as vacuum or viscous flow reactors can be used in ALD for non-planar and high surface area substrates. For the substrates with high aspect ratios, continuous flow processes sometimes require impractical lengths of exposure time for achieving full and uniform fillings of trenches because of the insufficient Knudsen flow of precursor gases. In a stop flow process, higher precursor concentration can be applied since it requires longer diffusion time to deposit on the trench surfaces. When using high-surface-area substrates, it is attractive to use dedicated reactor designs, since the use of conventional reactors will lead to longer deposition times and lower precursor efficiency.

1.5.2 Desalination Freshwater can be obtained from the ocean, sea and brackish water bodies through the desalination process. However, this process can be costly. In another hand, seawater accounts for about 97.5% of the water resources on earth. Desalination has become increasingly significant for water production in semi-arid coastal areas. It is no gainsaying that the world's growing population would need this water source to meet its growing demands. Several technologies are being used in the desalination process, the most desalination technologies at present are based on membrane separation through the reverse osmosis (RO) and thermal distillation (multi stage flash (MSF) and multi-effect distillation (MED). Reverse osmosis based on polymeric membranes has several challenges which include slow water transport and tremendous energy costs. Hence, the need for a method to resolve this issue and biomimetic membranes. An emerging technology has promising potentials to address the issues. This review paper will focus on the latest development of biomimetic based membranes.

1.6 Developments in ALD

Development of atomic layer deposition (ALD) processes, either to enable fabrication of new materials by ALD, as well as to improve existing ALD materials, is an ongoing effort within the ALD-field (as was also illustrated by our recent blog post with an overview of binary materials prepared by ALD). This also holds for the research performed by our group; a large part of our publications concern novel ALD processes. Speaking from personal perspective, I have set up ALD recipes for deposition of Cobalt (Co), Ruthenium (Ru), Aluminium Fluoride (AlF3) and Molybdenum Oxide (MoO3) during my time in the PMP group (which started back in 2012). Along the way I think I gained some knowledge on the subject of process development, which I would like to (or at least try to) share in this blog. I hope it can serve as a starting point for people who are new to ALD process development, or provide some additional perspectives for those we are more experienced.

1.7 Concluding Remarks:-

ALD has been a viable and widely utilized manufacturing method in the microelectronics industry. Currently, many research laboratories have access to reliable ALD tools, and the materials and processing options for ALD continue to expand. The growing field of plasmonics will increase the demand for new ALD processes to decorate various metallic surfaces at low temperatures. For the most part, existing applications in plasmonics and biotechnology have utilized Al2O3 or SiO2. In particular, metallic nano-structures that are over coated with SiO2 shells can easily incorporate lipid bilayer membranes, which can be very useful for applications in 64, 65 biomimetic sensing and membrane proteins research. Other materials such as HfO2 or TiO2, which have higher refractive indices, could also be employed. While ALD for metals also looks promising for applications in plasmonics, impurities derived from the precursors remain in the metal. Thus metal films deposited by ALD exhibit poorer electrical and optical properties compared with pure metals deposited by evaporation or sputtering. As summarized in previous sections, the requirements for coating, patterning, tuning, and protecting metallic nano-structures are indeed very demanding. Metal surfaces, which are often rough and chemically unstable, should be modified at low temperatures with ultra-thin, pinhole-free over layers. Conformal filling or complete encapsulation is required for nano-structures with extremely demanding aspect ratios. Finally, these ultra-thin films should act as a robust protection layer against harsh environments. ALD can readily satisfy all of these requirements and will continue to enable new and exciting applications.

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