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CHALLENGES AND OPPORTUNITIES IN ELECTROCHEMICAL ATOMIC LAYER DEPOSITION OF NOBLE METALS

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ABSTRACT

Electrochemical Atomic Layer Deposition (E-ALD) is a promising technique for depositing noble metals with atomic-level precision. However, like any emerging technology, it presents several challenges that must be addressed to fully exploit its potential. This study investigates the challenges and opportunities of Electrochemical Atomic Layer Deposition (E-ALD) of noble metals. The study identifies three major challenges in the E-ALD process, including control of deposition process, electrodeposition mechanism, and adhesion and stability. The control of the deposition process requires precise adjustment of deposition conditions to avoid defects and non-uniformity. The mechanism of electrodeposition of noble metals is complex and requires further investigation for the development of reliable and reproducible E-ALD processes. The adhesion and stability of the deposited layer on the substrate under different environmental conditions is another challenge that needs to be addressed. The study also reveals significant opportunities offered by E-ALD. The atomic-level precision of E-ALD can enable the fabrication of new materials with unique properties and functionalities. The versatility of E-ALD allows for the deposition of noble metals on a wide range of substrates, including metals, semiconductors, and insulators. E-ALD is also a cost-effective technique for depositing noble metals, as it uses a small amount of precursor and achieves high coverage with low thickness. This reduces the cost of materials and processing time, making E-ALD an attractive technique for various applications.

Keywords: Electrochemical Atomic Layer Deposition, Noble metals, Challenges, Atomic-level precision, Cost-effectiveness

INTRODUCTION

Electrochemical atomic layer deposition (E-ALD) is a promising technique for depositing thin films of noble metals such as ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), osmium (Os), iridium (Ir), platinum (Pt), and gold. This technique has attracted a lot of attention due to its ability to produce high-quality films with excellent control over film thickness, composition, and morphology [1]–[3]. E-ALD is an electrochemical process that involves the use of electrochemical reactions to deposit metal ions onto a substrate surface.

In E-ALD, the substrate is immersed in an electrolyte solution containing metal ions. A potential difference is applied between the substrate and a counter electrode, causing the metal ions to be reduced onto the substrate surface. The deposition process proceeds in a cyclic manner, where each cycle consists of a deposition step followed by a rinsing step. During the deposition step, the metal ions are reduced onto the substrate surface, forming a monolayer of metal atoms. The rinsing step involves the removal of excess electrolyte and by-products from the substrate surface, preparing the substrate for the next deposition cycle.



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One of the key advantages of E-ALD is its ability to deposit metal films with excellent conformality, meaning that the film thickness is uniform across complex three-dimensional surfaces [4]–[7]. This is due to the fact that E-ALD relies on self-limiting surface reactions, which ensure that only a single atomic layer is deposited per cycle. The deposition of each atomic layer is driven by the adsorption of metal ions onto the substrate surface, followed by the reduction of the metal ions into metal atoms. The thickness of the film can be controlled by adjusting the number of deposition cycles.

E-ALD has been successfully used for the deposition of various noble metals, including ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold. These metals are commonly used in various electronic and catalytic applications due to their unique properties. For example, platinum is widely used as a catalyst in fuel cells and catalytic converters due to its high catalytic activity towards oxygen reduction and oxidation reactions. Similarly, gold is used in various electronic applications due to its excellent electrical conductivity and resistance to corrosion.

Ruthenium is another noble metal that has attracted a lot of attention in recent years due to its unique electronic and catalytic properties. Ruthenium is a transition metal that belongs to the platinum group of metals and is known for its high corrosion resistance, high melting point, and excellent catalytic activity towards various reactions. E-ALD has been shown to be an effective technique for the deposition of ruthenium films with excellent conformality and uniformity. These films have been shown to exhibit excellent electrocatalytic activity towards various reactions, including hydrogen evolution and carbon dioxide reduction.

Rhodium is another noble metal that has attracted a lot of attention due to its unique catalytic properties. Rhodium is known for its high catalytic activity towards various reactions, including hydrogenation, isomerization, and oxidation reactions. E-ALD has been shown to be an effective technique for the deposition of rhodium films with excellent conformality and uniformity. These films have been used in various catalytic applications, including the hydrogenation of benzene and the oxidation of carbon monoxide.

Palladium is another noble metal that is widely used in various electronic and catalytic applications. Palladium is known for its excellent catalytic activity towards various reactions, including the hydrogenation of alkenes and the oxidation of carbon monoxide. E-ALD has been shown to be an effective technique for the deposition of palladium films with excellent conformality and uniformity. These films have been used in various catalytic applications, including the selective hydrogenation of acetylene and the electrocatalytic reduction of carbon dioxide.

Silver is another noble metal that has been widely used in various electronic and optical applications. Silver is known for its excellent electrical conductivity and optical properties, making it ideal for the fabrication of conductive films and optical coatings. E-ALD has been shown to be an effective technique for the deposition of silver films with excellent conformality and uniformity. These films have been used in various applications, including the fabrication of transparent conductive films and the production of surface-enhanced Raman spectroscopy (SERS) substrates.

Osmium is a relatively rare noble metal that is known for its high density and excellent catalytic properties. Osmium is often used as a co-catalyst in various catalytic reactions,

where it enhances the catalytic activity of other metals. E-ALD has been shown to be an effective technique for the deposition of osmium films with excellent conformality and uniformity. These films have been used in various catalytic applications, including the oxidation of alcohols and the hydrogenation of nitroarenes.

Iridium is another noble metal that is known for its unique electronic and catalytic properties. Iridium is often used as a catalyst in various reactions, including the hydrogenation of alkenes and the oxidation of water. E-ALD has been shown to be an effective technique for the deposition of iridium films with excellent conformality and uniformity. These films have been used in various catalytic applications, including the electrocatalytic oxidation of water to produce hydrogen.

Electrochemical atomic layer deposition (E-ALD) is a promising technique for the deposition of thin films of noble metals such as ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), osmium (Os), iridium (Ir), platinum (Pt), and gold [8], [9]. E-ALD offers excellent control over film thickness, composition, and morphology, making it ideal for various electronic and catalytic applications. The ability of E-ALD to produce films with excellent conformality and uniformity has enabled the fabrication of complex three-dimensional structures with high precision. As such, E-ALD is a powerful tool for the development of advanced materials and devices for various applications, including energy conversion, environmental remediation, and sensing.

CHALLENGES

Control of deposition process:

The electrodeposition atomic layer deposition (E-ALD) process is a complex and precise method of depositing individual atomic layers on a substrate. The success of this process is largely dependent on the precise control of the deposition conditions, which include deposition potential, temperature, and electrolyte concentration, substrate [7], [10]. Any deviation from these conditions can result in defects and non-uniformity in the deposited layer.

To begin with, the deposition potential plays a crucial role in the E-ALD process. Deposition potential refers to the voltage applied to the substrate during the deposition process. It is essential to maintain a constant deposition potential throughout the process to ensure a uniform and conformal metal layer. Any fluctuation or deviation in the deposition potential can result in defects such as pinholes, cracks, and non-uniform thickness of the deposited layer. Therefore, it is imperative to monitor and control the deposition potential carefully.

Moreover, the temperature during the deposition process is another crucial parameter that requires precise control. The temperature affects the mobility of the metal ions in the electrolyte, which can ultimately impact the nucleation and growth of the deposited layer. If the temperature is too low, the metal ions will have limited mobility, leading to poor adhesion and non-uniform thickness. On the other hand, if the temperature is too high, the metal ions can become too mobile, leading to the formation of dendrites, which are protruding metal structures that can cause short circuits in electronic devices [11], [12]. Therefore, it is essential to maintain a constant and precise temperature during the E-ALD process to ensure the quality and uniformity of the deposited layer.

Lastly, the electrolyte concentration is also an essential parameter that requires precise control during the E-ALD process. The electrolyte concentration affects the nucleation and growth of the deposited layer by controlling the number of metal ions available in the electrolyte. A high electrolyte concentration can lead to a high number of metal ions, resulting in rapid nucleation and growth of the deposited layer. However, it can also result in the formation of non-uniform layers and dendrites. On the other hand, a low electrolyte concentration can result in poor adhesion and non-uniform thickness of the deposited layer. Therefore, it is crucial to maintain a constant and precise electrolyte concentration during the E-ALD process to ensure a uniform and conformal metal layer.

The E-ALD process is a complex and precise method of depositing individual atomic layers on a substrate. The success of this process is largely dependent on the precise control of the deposition conditions, such as deposition potential, temperature, and electrolyte concentration [13], [14]. Any deviation in these conditions can lead to defects and non-uniformity in the deposited layer. Therefore, it is imperative to monitor and control these parameters carefully throughout the E-ALD process to ensure the quality and uniformity of the deposited layer.

Pb underpotential deposition is a process used in electrochemistry to deposit submonolayer amounts of lead atoms onto a metal surface and is commonly used in the production of electronic devices, such as batteries and solar cells, where it helps improve the performance of the final product [15]–[20]. However, despite its usefulness, lead (Pb) cannot be used in the semiconductor industry due to its toxicity concerns. Lead is a highly toxic heavy metal that can accumulate in the body over time, causing a wide range of health problems such as neurological damage and developmental disorders. Therefore, the use of lead in the semiconductor industry is strictly regulated, and alternative materials are being developed to replace it. One such alternative material is zinc (Zn), which plays a critical role in the development of barrierless interconnects for next-generation nodes using the e-ALD (atomic layer deposition) process. In the e-ALD process, thin layers of metal are deposited onto a substrate using a series of chemical reactions. Zn has emerged as a promising material for this process due to its low resistivity, high thermal stability, and excellent adhesion properties [21], [22]. Moreover, zinc is a relatively abundant and non-toxic element, making it an attractive alternative to lead.

Electrodeposition mechanism:

Electrodeposition, also known as electroplating, is the process of depositing a thin layer of metal onto a conductive substrate using an electric current [23]–[25]. This process is widely used in various industries, including electronics, aerospace, and automotive, to improve the surface properties of the substrate [26], [27]. Noble metals, such as gold, platinum, and silver, are often used in electrodeposition due to their unique properties, such as high conductivity, chemical stability, and corrosion resistance [28], [29]. However, the electrodeposition mechanism of noble metals is not well understood, and their electrochemical behavior can be complex.

The electrochemical behavior of noble metals during electrodeposition can be influenced by several factors, including the presence of impurities in the electrolyte, the surface chemistry of the substrate, and the deposition potential. Impurities in the electrolyte can affect the electrochemical reaction by altering the concentration of the metal ions in the

solution or by introducing competing reactions that can interfere with the deposition process. Therefore, it is essential to use high-quality electrolytes with low impurity levels to achieve reliable and reproducible electrodeposition processes.

The surface chemistry of the substrate is also a crucial factor that can influence the electrodeposition mechanism of noble metals. The substrate's surface properties, such as its roughness, composition, and crystallographic orientation, can affect the adsorption and diffusion of metal ions onto the substrate's surface. For example, a rough substrate surface can provide more surface area for metal ion adsorption, leading to a higher deposition rate. On the other hand, a smooth surface can facilitate the formation of a more uniform and dense metal film. Therefore, it is essential to optimize the substrate surface properties to achieve the desired deposition characteristics.

The deposition potential is another critical factor that can affect the electrodeposition mechanism of noble metals. The deposition potential is the voltage applied to the substrate during the electrodeposition process, and it determines the rate and morphology of the deposited metal film. However, the optimal deposition potential can vary depending on several factors, including the metal ion concentration, the substrate's surface chemistry, and the presence of impurities in the electrolyte. Therefore, it is crucial to determine the appropriate deposition potential for a particular electrodeposition process to achieve the desired deposition characteristics.

Despite the importance of these factors, the electrodeposition mechanism of noble metals is still not well understood. The electrochemical behavior of noble metals during electrodeposition can be complex, and it can involve several simultaneous processes, such as metal ion adsorption, reduction, and nucleation. Therefore, a better understanding of the electrodeposition mechanism of noble metals is crucial for developing reliable and reproducible electrodeposition processes.

One approach to studying the electrodeposition mechanism of noble metals is to use in-situ characterization techniques, such as electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). EIS can provide information on the electrical properties of the electrodeposition process, such as the charge transfer resistance and the double layer capacitance, while SEM can provide information on the morphology and structure of the deposited metal film. By combining these techniques, researchers can obtain a better understanding of the electrodeposition mechanism of noble metals.

Another approach to studying the electrodeposition mechanism of noble metals is to use computational modeling techniques. Computational modeling can provide insights into the fundamental processes involved in the electrodeposition mechanism, such as the adsorption and diffusion of metal ions onto the substrate's surface, the nucleation and growth of metal nuclei, and the coalescence of metal nuclei into a continuous film. By simulating these processes, researchers can identify the key factors that influence the electrodeposition mechanism and design new electrodeposition processes with improved performance. The electrodeposition mechanism of noble metals is a complex and not well-understood process. The electrochemical behavior of noble metals can be influenced by several factors, including the presence of impurities in the electrolyte, the surface chemistry of the substrate, and the deposition potential. Therefore, it is crucial to optimize these factors to achieve reliable and reproducible electrodeposition processes.

Adhesion and stability:

The deposition of thin films is an essential process in many industrial and scientific applications. These films can be made from a variety of materials, including metals, oxides, and semiconductors. One of the key challenges in depositing thin films is achieving uniform and continuous coverage on the substrate. This challenge is particularly acute when working with noble metals, which have a high surface energy and tend to form islands or clusters rather than forming a continuous layer.

Noble metals, such as gold, silver, and platinum, have unique properties that make them desirable for many applications. These metals are resistant to corrosion and oxidation, are excellent conductors of electricity and heat, and have a high melting point. However, these properties also make it challenging to deposit them as thin films. When deposited onto a substrate, noble metals tend to form islands or clusters rather than forming a continuous layer. This behavior is due to the high surface energy of these metals, which causes them to minimize their surface area by clustering together.

Achieving uniform and continuous coverage of a substrate with a noble metal film requires careful control over the deposition process. One approach to achieving this is to use a technique known as physical vapor deposition (PVD), which involves heating the metal in a vacuum chamber until it vaporizes and condenses onto the substrate. By controlling the temperature and pressure in the chamber, it is possible to deposit a continuous layer of metal onto the substrate.

Another challenge in depositing thin films is ensuring that the deposited layer adheres strongly to the substrate. Adhesion is critical because it determines the durability and reliability of the deposited layer. If the layer does not adhere well to the substrate, it can peel or flake off, leading to failure of the device or component being fabricated. Adhesion is particularly important when working with noble metals because they tend to form weak adhesion bonds with many substrates.

Several factors influence the adhesion of a deposited layer to the substrate. One of the most important is the cleanliness of the substrate. Any contaminants on the substrate surface can interfere with the adhesion process and weaken the bond between the metal and the substrate. Therefore, it is essential to clean the substrate thoroughly before depositing the metal layer. This can be done using a variety of techniques, including solvent cleaning, plasma cleaning, and ion bombardment.

The surface roughness of the substrate can also affect the adhesion of the deposited layer. A rough surface provides more surface area for the metal to bond with, leading to stronger adhesion. However, if the surface is too rough, it can interfere with the formation of a continuous metal layer, leading to the formation of islands or clusters.

The choice of deposition technique can also impact the adhesion of the deposited layer. For example, PVD techniques typically provide good adhesion because the metal atoms have high kinetic energy and can form strong bonds with the substrate. In contrast, techniques such as electroplating can result in weaker adhesion because the metal ions have lower kinetic energy and are more prone to forming weak adhesion bonds.

In addition to achieving good adhesion, the stability of the deposited layer under various environmental conditions is also a critical factor. The stability of the layer is influenced by several factors, including the chemical and physical properties of the metal, the composition of the substrate, and the environmental conditions to which the layer is exposed.

One of the most significant factors affecting the stability of a deposited layer is the exposure to air and moisture. Noble metals are particularly susceptible to corrosion when exposed to air and moisture, which can degrade the performance of the device or component being fabricated. To minimize the effects of corrosion, it is essential to protect the deposited layer from exposure to air and moisture. This can be done by encapsulating the layer with a protective coating or by storing the device or component in a dry environment.

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OPPORTUNITIES

Atomic-level precision:

Atomic-level precision is a term used to describe the ability to manipulate matter at the scale of individual atoms. This level of precision is essential for the fabrication of new materials with unique properties and functionalities. One technique that offers atomic-level precision is Electron-Assisted Atomic Layer Deposition (E-ALD).

E-ALD is a thin-film deposition technique that utilizes a series of self-limiting surface reactions to deposit material onto a substrate. Unlike other deposition techniques, E-ALD offers unparalleled control over the thickness, composition, and morphology of deposited layers. This level of control is made possible by the use of an electron beam, which assists in the surface reactions and ensures that the deposited layers are uniform, conformal, and of precise thickness.

The ability to deposit noble metals with atomic-level precision is a significant advantage of E-ALD. Noble metals, such as gold, silver, and platinum, are highly desirable in many applications due to their unique properties. For example, gold is an excellent conductor of electricity and is highly resistant to corrosion, making it an ideal material for use in electronics and medical devices. Silver is also an excellent conductor of electricity and is commonly used in high-performance electronics [10]. Platinum, on the other hand, is an excellent catalyst and is used in many industrial processes.

By depositing noble metals with atomic-level precision, E-ALD can enable the fabrication of new materials with unique properties and functionalities. For example, by depositing multiple layers of different noble metals, it is possible to create alloys with tailored properties. This level of control over the composition and morphology of materials is essential for the development of new technologies, such as advanced sensors, high-performance electronics, and efficient energy conversion devices.

Another advantage of E-ALD is its ability to deposit conformal layers. Conformal deposition is critical in many applications, such as in the fabrication of high-aspect-ratio structures or in the creation of uniform coatings on complex geometries. E-ALD can deposit conformal layers with atomic-level precision, ensuring that the entire surface is coated uniformly.

The uniformity of deposited layers is also essential for many applications. For example, in the fabrication of high-performance electronics, even small variations in layer thickness can lead to significant changes in device performance. With E-ALD, it is possible to deposit layers with a precision of a few angstroms, ensuring that the layers are uniform and the device performance is consistent.

In addition to its precision, E-ALD is also a highly scalable technique. It can be used to deposit layers on large-area substrates, making it suitable for industrial-scale applications. This scalability, combined with its precision, makes E-ALD an attractive technique for the development of new technologies.

The use of E-ALD is not limited to the deposition of noble metals. It can also be used to deposit other materials, such as oxides, nitrides, and sulfides. By depositing these materials with atomic-level precision, it is possible to create new materials with unique properties and functionalities. For example, by depositing oxides with different compositions and thicknesses, it is possible to create materials with tailored electronic properties.

E-ALD is a powerful technique that offers atomic-level precision in the deposition of thin films. Its ability to deposit uniform, conformal, and precise thickness layers of noble metals enables the fabrication of new materials with unique properties and functionalities [30]–[33]. This level of control over the composition and morphology of materials is essential for the development of new technologies, and E-ALD is well-suited for industrial-scale applications. With the continued development of E-ALD and other atomic-level precision techniques, the possibilities for the creation of new materials and technologies are endless.

Versatility:

Electrochemical Atomic Layer Deposition is a highly versatile method that can be utilized for the deposition of noble metals on an extensive range of substrates. With its ability to deposit metals on metals, semiconductors, and insulators, E-ALD has quickly become a sought-after method for a wide variety of applications. ALE is a critical step in the fabrication of semiconductor devices, as it enables the creation of extremely small features with high accuracy and uniformity. Unlike other etching methods that remove material indiscriminately, ALE removes a single layer of atoms at a time, leaving the underlying layers intact. This level of precision is crucial for the creation of modern integrated circuits and other semiconductor devices, where the size of the features is measured in nanometers.

ALD (atomic layer deposition) and ALE (atomic layer etching) are complementary processes that work together to create the intricate structures needed for advanced semiconductor devices [19], [34], [35]. ALD involves depositing a thin layer of material onto a substrate, one atomic layer at a time, while ALE removes thin layers of material with atomic precision. Together, these processes enable the creation of extremely small and complex structures, such as the transistors and memory cells used in modern microprocessors.

As the semiconductor industry continues to push the boundaries of what is possible with ever-smaller feature sizes, ALD and ALE will become increasingly important. These techniques will be the workhorse for the industry, enabling the creation of next-generation devices that are faster, more efficient, and more powerful than ever before.

One of the primary advantages of E-ALD is its ability to deposit noble metals on a range of substrates. Noble metals, such as platinum and gold, are frequently utilized in numerous applications due to their excellent conductivity and unique physical and chemical properties. However, the challenge with depositing noble metals is finding a method that is versatile enough to apply them to different substrates. E-ALD is one such technique that provides that versatility.

The ability to deposit noble metals on various substrates is particularly beneficial in applications such as catalysis, where the choice of substrate is essential. For example, in fuel cells, the electrodes are frequently made of platinum, but the substrate can vary, depending on the application. E-ALD enables platinum deposition on a range of substrates, allowing for greater flexibility in electrode design and optimization. The ability to use E-ALD on different substrates also opens the door for the development of new applications that may have previously been unfeasible.

Another advantage of E-ALD is its ability to create atomically precise coatings. E-ALD deposits materials one atomic layer at a time, ensuring that the deposited layer is uniform and defect-free. This precision enables the creation of ultra-thin coatings, which are crucial in numerous applications, such as electronics and optics. The uniformity of the deposited layers is also essential in catalysis, as it ensures that the catalyst is active throughout the entire surface area, improving its efficiency.

E-ALD is not only versatile but also provides an environmentally friendly option for noble metal deposition. The technique utilizes an electrolyte solution, which is composed of a precursor that contains the noble metal ion and a reducing agent. The reducing agent facilitates the reduction of the metal ions, allowing for the deposition of the noble metal on the substrate. Unlike traditional deposition techniques, which often require the use of toxic chemicals and high temperatures, E-ALD is performed at low temperatures and without the need for toxic chemicals. This makes it a more sustainable and environmentally friendly option for noble metal deposition.

In addition to its environmental benefits, the low-temperature deposition process also allows for the deposition of noble metals on temperature-sensitive substrates such as organic materials. The ability to deposit metals on organic materials opens up a range of applications, such as flexible electronics and biosensors, which require metal deposition on these substrates.

E-ALD's versatility also extends to its scalability. The technique can be used to deposit materials on a small scale, such as in research labs, but can also be scaled up for industrial applications. This scalability makes E-ALD an attractive option for industries such as electronics, where the need for precise and uniform coatings is crucial. The ability to scale up E-ALD deposition also allows for the development of new applications and the optimization of existing ones. E-ALD is a highly versatile technique that offers numerous benefits for the deposition of noble metals. Its ability to deposit metals on a range of substrates, create atomically precise coatings, and provide an environmentally friendly option for deposition makes it an attractive option for a wide variety of applications. Its scalability further adds to its appeal, as it allows for the optimization of existing applications and the development of new ones.

E-ALD's versatility is not limited to noble metals deposition; it can also be used for other materials such as oxides, nitrides, and sulfides. The technique's ability to create uniform and defect-free coatings makes it a useful tool in the development of materials for a wide range of applications. For instance, in the field of photovoltaics, E-ALD has been utilized to deposit materials such as zinc oxide, which is an essential component in solar cells. The precise and uniform deposition of zinc oxide using E-ALD has led to improved cell efficiency and performance.

Furthermore, E-ALD can also be utilized in the development of new nanomaterials. By depositing multiple layers of different materials, researchers can create complex structures with unique properties. This approach has been used in the development of new catalysts, which can be used in various chemical reactions. The precise control over the deposition process provided by E-ALD makes it an ideal technique for the creation of these complex structures.

Cost-effectiveness:

E-ALD or Atomic Layer Deposition (ALD) is a highly effective and efficient technique for the deposition of thin films of various materials. It has gained significant attention in the industry due to its numerous advantages over conventional techniques. One of the major advantages of E-ALD is its cost-effectiveness.

Conventional techniques for depositing noble metals, such as sputtering and evaporation, are expensive due to the use of a large amount of precursor materials. These materials are often very expensive, and a large amount of them is required to achieve a high level of coverage. E-ALD, on the other hand, uses a small amount of precursor material, which significantly reduces the cost of deposition. This is because E-ALD is a surface-controlled process that utilizes a self-limiting mechanism, which ensures that the precursor is used efficiently, reducing wastage. The process of self-limiting adsorption occurs because the precursor gas molecules are introduced into the chamber in pulses, allowing each molecule to react with only one surface layer at a time, forming a monolayer before saturation. This results in highly uniform, conformal thin films of noble metals that have a low thickness.

The ability to achieve high coverage with low thickness is another major factor that contributes to the cost-effectiveness of E-ALD. E-ALD can achieve high coverage with low thickness due to the surface-controlled nature of the process, which allows for the precise control of film thickness. The process can be precisely tuned to achieve the desired film thickness and coverage, which is essential for industries that require highly uniform films with precise thicknesses [36], [37].

The ability to achieve high coverage with low thickness is also beneficial for reducing processing time. Since the process of E-ALD is highly controlled, it requires less processing time compared to conventional techniques. The deposition of thin films by E-ALD can be completed in a relatively short amount of time, which reduces the cost of processing and increases the throughput of the system. This is especially important for industries that require high volumes of products with precise deposition requirements.

E-ALD is a highly attractive technique for industries that require the deposition of noble metals for their products. The cost-effectiveness of E-ALD makes it an excellent choice for industries that require large volumes of high-quality thin films. Some examples of

industries that can benefit from E-ALD include the semiconductor industry, where thin films of noble metals such as platinum, gold, and silver are used for their electrical conductivity and corrosion resistance, and the biomedical industry, where thin films of noble metals such as gold and silver are used for their antibacterial properties.

E-ALD is a highly effective and efficient technique for the deposition of thin films of various materials, especially noble metals. The cost-effectiveness of E-ALD is primarily due to the use of a small amount of precursor and the ability to achieve high coverage with low thickness. The use of a small amount of precursor helps to reduce the cost of materials, while achieving high coverage with low thickness can reduce the processing time. This makes E-ALD a highly attractive technique for industries that require the deposition of noble metals for their products. The ability to precisely control film thickness and achieve highly uniform films makes E-ALD an excellent choice for industries that require high volumes of products with precise deposition requirements [38], [39].

CONCLUSION

Electrochemical atomic layer deposition (E-ALD) has emerged as a promising technique for the deposition of noble metals with atomic-scale precision, uniformity, and conformality. This technique involves the deposition of thin films of noble metals by alternating the reduction and oxidation reactions of the metal ions in an electrolyte solution on the surface of a substrate. E-ALD has garnered significant interest in recent years due to its ability to produce thin films of noble metals with unprecedented control over their properties, which makes it an attractive option for the fabrication of nanoscale devices and sensors.

Despite its potential, E-ALD of noble metals still faces several challenges that must be addressed to make it a viable industrial process. One significant challenge is controlling the deposition rate and thickness of the films. This challenge arises because the deposition rate is dependent on several factors such as the concentration of metal ions in the electrolyte, the applied potential, the temperature, and the pH of the solution. Any deviation from the optimal conditions can result in non-uniform films or films with poor adhesion to the substrate. Additionally, choosing the right electrolyte for the deposition of noble metals is crucial since the electrolyte properties have a significant impact on the quality and properties of the deposited films.

Another challenge is maintaining the stability of the E-ALD process. The deposition process is sensitive to changes in the reaction conditions, such as temperature, pH, and metal concentration. Any variation in these parameters can cause a breakdown in the reaction mechanism and lead to the formation of unwanted products or incomplete films. Moreover, scalability and cost are also significant challenges that must be addressed for the industrial implementation of E-ALD of noble metals. The cost of the equipment, electrolytes, and metal precursors can be prohibitively high, and the scalability of the process is limited by the complexity of the equipment and the difficulties in maintaining the process stability at larger scales.

Despite the challenges, E-ALD of noble metals presents several opportunities that make it an attractive technique for the fabrication of nanoscale devices and sensors. One significant advantage is the atomic-scale precision it offers. E-ALD can deposit layers with thicknesses in the sub-nanometer range, which makes it ideal for the fabrication of ultrathin

films and interfaces. Additionally, E-ALD can provide conformal and uniform deposition over complex geometries, which is crucial for the fabrication of devices with high aspect ratios, such as microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS). Moreover, E-ALD can tailor the surface properties of the deposited films by adjusting the reaction conditions, which makes it an attractive option for applications such as surface-enhanced Raman spectroscopy (SERS) and catalysis.

The versatility of E-ALD of noble metals is another significant advantage. The technique can deposit a wide range of noble metals such as gold, platinum, and palladium, which have unique properties that make them suitable for different applications. For instance, gold is an excellent material for plasmonic applications due to its ability to support surface plasmons at visible frequencies. On the other hand, platinum is a preferred material for catalysis applications due to its high activity and stability in harsh environments. Furthermore, E-ALD can also deposit alloys and composite materials, which can offer additional properties such as improved mechanical strength and thermal stability.

E-ALD of noble metals is a promising technique for the fabrication of nanoscale devices and sensors due to its atomic-scale precision, conformal and uniform deposition, tailored surface properties, and versatility. However, the technique still faces several challenges that must be addressed to make it a viable industrial process. The development of new electrolytes, deposition techniques, and process control strategies can help to overcome the challenges associated with E-ALD of noble metals. Additionally, advancements in nanofabrication techniques and equipment can help to improve the scalability and cost-effectiveness of the process, making it more attractive for industrial applications.

One potential approach to overcome the challenges of E-ALD is to employ in-situ monitoring techniques to provide real-time feedback on the deposition process. For instance, spectroscopic techniques such as in-situ infrared spectroscopy and surface-enhanced Raman spectroscopy can provide information on the chemical composition and structure of the deposited films. Furthermore, electrochemical impedance spectroscopy can provide information on the electrical properties of the films, which can be used to monitor the growth rate and thickness of the films. Such techniques can help to optimize the reaction conditions and ensure the uniformity and conformity of the deposited films.

Another potential solution is to develop new electrolytes that are more stable and have better control over the deposition rate and thickness. For instance, the use of ionic liquids as electrolytes can provide several advantages over traditional aqueous electrolytes. Ionic liquids have lower vapor pressure and higher conductivity than traditional electrolytes, which can enhance the stability and control of the deposition process. Additionally, ionic liquids can dissolve a wide range of metal precursors, which can expand the range of metals that can be deposited using E-ALD.

The development of new deposition techniques can also help to overcome the challenges associated with E-ALD of noble metals. For instance, the use of electroless deposition techniques can provide an alternative approach to depositing noble metals with atomic-scale precision. Electroless deposition involves the deposition of metals by a redox reaction between a reducing agent and metal ions in a solution. The reaction occurs spontaneously without the need for an external potential, which can simplify the deposition process and reduce the complexity of the equipment. Additionally, electroless deposition can deposit a

wide range of metals and alloys, which can expand the range of applications for nanofabrication.

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