

Precise Deposition of Thin Films using Electrochemical Atomic Layer Deposition: Applications in Energy Storage, Catalysis, and Microelectronics

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ABSTRACT

This research investigates the application of Electrochemical Atomic Layer Deposition (E-ALD) technique for thin-film deposition in various fields. The study finds that E-ALD provides precise control over the deposition of thin films, which can significantly enhance the performance and stability of various devices. The results indicate that E-ALD can be applied for energy storage, corrosion protection, catalysis, optoelectronics, and microelectronics. Specifically, the research demonstrates that E-ALD can be utilized to deposit thin films of electrode materials for energy storage applications, providing uniform and continuous coverage to enhance device performance and stability. Moreover, E-ALD can be used to deposit thin films of corrosion-resistant materials on metal substrates for effective corrosion protection. Additionally, the study shows that E-ALD can deposit thin films of catalytic materials, which significantly improve the catalytic activity and selectivity of these materials. E-ALD also demonstrates potential for use in optoelectronic devices, such as solar cells and light-emitting diodes, to improve device performance and stability. Lastly, E-ALD can deposit thin films of materials for use in microelectronics, such as thin-film transistors and capacitors, improving their performance and reliability. These findings highlight the potential of E-ALD as a versatile technique for precise deposition of thin films in various fields.

INTRODUCTION

Thin Film Deposition (TFD) is a critical technology used in the manufacturing of various industrial products. The process involves the deposition of a thin layer of material, typically ranging from a few nanometers to a few micrometers, on a substrate surface [1]–[3]. This deposition can occur through various methods, including physical vapor deposition (PVD), chemical vapor deposition (CVD), and atomic layer deposition (ALD). PVD and CVD are the most common techniques used in TFD, and they both involve the deposition of materials in a vacuum chamber.

In PVD, a material is vaporized using various techniques, such as evaporation or sputtering, and then condensed onto a substrate surface. This process can be done at low or high pressures, depending on the application. In contrast, CVD involves the chemical reaction of gas-phase precursors that are adsorbed onto a substrate surface to form a solid material. The reaction can be initiated through thermal or plasma-assisted methods.

Thin Film Deposition has enabled the development of various industrial products, including semiconductor devices, solar panels, and optical devices. The semiconductor industry uses TFD to manufacture integrated circuits and memory chips, where the thin films act as conductive, insulating, or barrier layers. Solar panels also rely on TFD to deposit thin films of semiconductors, such as cadmium telluride or copper indium gallium selenide, onto a substrate surface to generate electricity. Optical devices, such as anti-reflection coatings and optical filters, use TFD to deposit thin films of dielectric materials onto glass or plastic surfaces [4], [5].

Electrochemical Atomic Layer Deposition (E-ALD) is an advanced technique that enables precise deposition of thin films on substrates. This method uses an electrochemical reaction to deposit solid-state material in a sequential and controlled manner. Unlike conventional Atomic Layer Deposition (ALD) processes, E-ALD does not require hazardous and expensive precursor gases. Instead, E-ALD relies on a solution containing an electrochemically active compound to deposit the material.

Underpotential deposition (UPD) is a powerful technique used in electrochemical atomic layer deposition (e-ALD) to deposit a monolayer of a metal on a substrate. In UPD, a metal electrode is polarized at a potential lower than the thermodynamic potential of the metal, resulting in the deposition of submonolayer amounts of metal on the electrode surface. This process allows for the formation of a uniform and controlled metal layer, which can be used as a template for the subsequent deposition of another metal layer, resulting in the formation of a multilayer structure. In e-ALD, UPD has been used to deposit copper (Cu), lead (Pb), and zinc (Zn) on various substrates, including metals, semiconductors, and insulators [6]. Copper (Cu), lead (Pb), and zinc (Zn) are commonly used metals that can be deposited using UPD in e-ALD. UPD of Cu has been particularly useful for the formation of a template for the subsequent deposition of other metals such as palladium (Pd) and platinum (Pt), resulting in the formation of multilayer structures that can be used in various applications, including catalysis and electrocatalysis. UPD of Pb and Zn has also been

used to form templates for the subsequent deposition of other metals, resulting in the formation of multilayer structures that can be used in various applications, including electrochemical sensing and hydrogen storage.

Electrochemical Atomic Layer Deposition (E-ALD) offers a low-cost, environmentally friendly, and scalable approach for the precise fabrication of semiconductor interconnect materials [7]–[9]. This process involves the sequential deposition of atomic layers using an electrochemical reaction. E-ALD is a form of Atomic Layer Deposition (ALD) and is a variant of conventional ALD processes that rely on chemical reactions between gaseous precursors. In E-ALD, a solid-state material is deposited from a solution containing an electrochemically active compound, and the deposition is precisely controlled by a potential control system.

E-ALD is a cost-effective and scalable approach to depositing atomically precise films of metals such as copper, cobalt, tungsten, and other materials that are widely used in the fabrication of semiconductor devices [10]–[12]. The thickness of the deposited films can be precisely controlled, resulting in high-quality, uniform films that can be produced over large areas. Additionally, E-ALD can be carried out at relatively low temperatures, making it possible to fabricate interconnect materials on heat-sensitive substrates.

The E-ALD technique offers several advantages over conventional ALD processes, including the elimination of costly and hazardous precursor gases and the ability to produce high-quality, uniform films over large areas at low temperatures. Additionally, E-ALD has been found to be a cost-effective approach to producing interconnect materials for semiconductor devices.

One of the primary applications of E-ALD is in the fabrication of semiconductor interconnect materials [10], [12]–[16]. Interconnects are used to connect different parts of a semiconductor device, and the performance of the device depends largely on the quality and precision of the interconnect material. E-ALD allows for the deposition of atomically precise thin films of materials such as copper, cobalt, tungsten, and other metals that are commonly used in interconnects. This technique also provides precise control over the thickness of the deposited films, resulting in uniform and high-quality films. E-ALD is an innovative technique that offers a cost-effective, environmentally friendly, and scalable approach for the precise fabrication of semiconductor interconnect materials. With the increasing demand for high-performance and energy-efficient semiconductor devices, E-ALD is likely to become

a critical technology in the field of material science, enabling the development of more advanced and efficient devices.

APPLICATIONS

Energy storage:

E-ALD is an important technique for energy storage applications, such as batteries and supercapacitors, as it provides precise control over the film thickness and composition. Batteries and supercapacitors are important energy storage devices that play a crucial role in modern society. These devices are used in a wide range of applications, from portable electronic devices to electric vehicles and renewable energy systems. In order to improve the performance and stability of these devices, it is necessary to develop new electrode materials and improve the deposition techniques used to fabricate them. E-ALD is one such technique that has been shown to be effective in depositing high-quality films of electrode materials.

E-ALD provides precise control over the film thickness and composition. This is achieved by controlling the number of reaction cycles used to deposit the material. The use of E-ALD allows for the deposition of films with a thickness of only a few nanometers, which is essential for the fabrication of high-performance energy storage devices. The ability to precisely control the film composition is also important, as it allows for the fabrication of complex layered materials that can improve the performance of these devices.

The use of E-ALD to deposit electrode materials can improve the performance and stability of energy storage devices in a number of ways. For example, the precise control of film thickness can improve the electrochemical performance of the device. This is because the electrochemical properties of the material are strongly influenced by its thickness, and a uniform thickness is essential for the proper functioning of the device [17], [18]. Additionally, the use of E-ALD can improve the stability of the device by reducing the likelihood of defects and other structural imperfections that can lead to device failure.

E-ALD can deposit films of complex layered materials. These materials can be designed to have specific electrochemical properties that are tailored to the requirements of the energy storage application. For example, layered materials can be designed to have high capacity, fast charge and discharge rates, and long cycle life. The use of E-ALD allows for the precise control of the composition and thickness of each layer, which is essential for the fabrication of these materials.

In addition to its advantages in electrode material deposition, E-ALD also has some limitations that must be taken into account. One limitation is the deposition rate of E-ALD is typically slow, which can limit the scalability of the technique. Despite these limitations, E-ALD is a powerful technique for the deposition of thin films of electrode materials on substrates for energy storage applications. The precise control of film thickness and composition provided by E-ALD can improve the performance and stability of these devices [19], [20]. The use of E-ALD can also enable the fabrication of complex layered materials that can be tailored to the specific requirements of the energy storage application.

Corrosion protection:

Corrosion is a natural process that occurs when metal materials react with their environment, leading to a deterioration of their properties over time. This process can cause significant damage and weaken the structural integrity of metal components in a variety of industries, from automotive to aerospace, infrastructure to electronics. To combat this issue, scientists and engineers have developed a range of corrosion protection methods, including coatings, inhibitors, and alloys [21]–[23].

One promising approach to corrosion protection is the use of atomic layer deposition (ALD), a thin-film deposition technique that allows for precise control over film thickness, composition, and structure. Recently, an extension of ALD, called electrochemical atomic layer deposition (E-ALD), has been developed, which combines the benefits of both electrochemical and ALD processes. E-ALD can be used to deposit thin films of corrosion-resistant materials on metal substrates, providing protection against corrosion.

The key advantage of using E-ALD for corrosion protection is that it allows for the deposition of uniform and continuous thin films. This is crucial for effective corrosion protection since any gaps or defects in the film can leave the underlying metal substrate vulnerable to corrosion. The thin films produced by E-ALD are typically only a few nanometers thick, which means that they do not significantly alter the properties of the metal substrate, such as its mechanical strength or conductivity.

The E-ALD process involves the sequential exposure of a metal substrate to a precursor solution and an electrolyte solution, with each exposure followed by a rinse step. The precursor solution contains the metal species that will be deposited onto the substrate, while the electrolyte solution provides the necessary electrons for the

electrochemical reaction. The thin films produced by E-ALD can be composed of a range of materials, including oxides, nitrides, and metals, depending on the choice of precursor and electrolyte.

One of the most promising applications of E-ALD for corrosion protection is in the aerospace industry, where metal components are exposed to a wide range of harsh environments, including high humidity, salt spray, and temperature extremes. Corrosion of these components can lead to costly maintenance and repair, as well as safety risks. By depositing thin films of corrosion-resistant materials onto these components using E-ALD, it is possible to extend their service life and reduce the need for frequent maintenance.

Another potential application of E-ALD for corrosion protection is in the automotive industry. Corrosion of automotive components can lead to reduced performance and safety issues, as well as decreased resale value. By using E-ALD to deposit corrosion-resistant films onto these components, manufacturers can improve the durability and reliability of their products, as well as enhance their aesthetic appeal.

In addition to its use in corrosion protection, E-ALD has other potential applications in the fields of electronics, energy storage, and catalysis. For example, E-ALD can be used to deposit thin films of high-k dielectric materials onto semiconductor substrates, which can improve the performance of electronic devices. It can also be used to deposit thin films of electrode materials onto energy storage devices, such as batteries and capacitors, which can enhance their efficiency and lifespan. Furthermore, E-ALD can be used to deposit thin films of catalyst materials onto substrates, which can improve the efficiency of chemical reactions and reduce the need for expensive catalysts.

Despite its potential advantages, E-ALD also has some limitations and challenges that need to be addressed. One of the main challenges is the need to optimize the deposition parameters, such as the choice of precursor and electrolyte, as well as the deposition temperature, time, and voltage. These parameters can have a significant impact on the properties of the deposited thin films, such as their composition, structure, and adhesion. Therefore, careful optimization is necessary to ensure the production of high-quality and effective corrosion-resistant films.

Another challenge is the scalability of the E-ALD process. While the technique has shown promising results in laboratory settings, its industrial-scale implementation

requires the development of cost-effective and efficient deposition systems. In addition, the production rate of E-ALD is typically slower than other deposition techniques, such as chemical vapor deposition (CVD) or physical vapor deposition (PVD), which can limit its practical applications.

To overcome these challenges, researchers are exploring various approaches to enhance the performance and scalability of E-ALD. For example, some studies have investigated the use of alternative deposition modes, such as pulsed electrodeposition, to improve the deposition rate and efficiency of E-ALD. Other studies have focused on the development of novel precursor and electrolyte solutions that can enhance the properties of the deposited films. Furthermore, advances in the design and fabrication of deposition systems can help improve the scalability and cost-effectiveness of E-ALD.

E-ALD has emerged as a promising approach to corrosion protection by allowing the deposition of uniform and continuous thin films of corrosion-resistant materials onto metal substrates. Its potential applications are vast, ranging from aerospace and automotive industries to electronics and energy storage. However, its industrial-scale implementation requires the development of cost-effective and efficient deposition systems and the optimization of deposition parameters. With continued research and development, E-ALD can offer a viable solution to combat corrosion and improve the durability and reliability of metal components in various industries.

Catalysis:

Catalysis is a process that accelerates a chemical reaction by providing an alternative pathway for the reaction to proceed. It is an important area of study with a wide range of applications, including industrial production of chemicals, pharmaceuticals, and energy conversion. Catalytic materials play a crucial role in catalysis, and the development of new materials with enhanced catalytic properties is an ongoing research area.

E-ALD, or Atomic Layer Deposition, is a thin-film deposition technique that allows for precise control over film thickness and composition. It is a highly versatile technique that has found applications in various fields, including electronics, optics, and energy. In recent years, researchers have explored the use of E-ALD for the deposition of catalytic materials on substrates.

One of the key advantages of using E-ALD for catalytic material deposition is the ability to achieve precise control over film thickness and composition. This is crucial for achieving optimal catalytic performance, as even minor variations in film thickness or composition can have a significant impact on the catalytic activity and selectivity of the material. E-ALD allows for the deposition of uniform, conformal films with sub-nanometer precision, making it an ideal technique for achieving this level of control.

Another advantage of using E-ALD for catalytic material deposition is the ability to deposit materials on a wide range of substrates. This is important as different substrates may be required for different catalytic applications. For example, in the production of hydrogen fuel, catalytic materials may need to be deposited on a conductive substrate to facilitate electron transfer. E-ALD can be used to deposit catalytic materials on a wide range of substrates, including conductive and non-conductive materials, making it a highly versatile technique.

One specific application of E-ALD for catalytic material deposition is in the production of fuel cells. Fuel cells are electrochemical devices that convert the chemical energy of a fuel, such as hydrogen, into electrical energy. Catalytic materials play a crucial role in the functioning of fuel cells, as they facilitate the reactions that occur at the fuel cell electrodes. E-ALD can be used to deposit catalytic materials on the electrodes of a fuel cell, improving the catalytic activity and selectivity of the materials.

In addition to fuel cells, E-ALD can also be used for catalytic material deposition in a wide range of other applications. For example, catalytic materials deposited using E-ALD can be used in the production of chemicals and pharmaceuticals, where they can improve the efficiency of chemical reactions and reduce the amount of waste generated. They can also be used in the production of renewable energy, such as in the catalytic conversion of biomass into biofuels.

The use of E-ALD for catalytic material deposition is still a relatively new area of research, and there is much work to be done in order to fully understand the potential of this technique. However, early studies have shown promising results, with improved catalytic activity and selectivity observed for materials deposited using E-ALD compared to those deposited using other techniques.

Overall, E-ALD has the potential to revolutionize the field of catalysis by enabling the deposition of highly precise, uniform, and conformal thin films of catalytic materials on a wide range of substrates. This could lead to the development of new, more efficient catalytic materials with a wide range of applications in various fields, including energy, chemical production, and pharmaceuticals.

Optoelectronics:

Optoelectronics is a rapidly growing field that has seen significant advances in recent years. Optoelectronic devices are used in a wide range of applications, including communication, sensing, imaging, and lighting. Some of the most widely used optoelectronic devices include solar cells and light-emitting diodes (LEDs). These devices rely on the precise deposition of thin films of materials to function effectively. E-ALD, or Electron-Enhanced Atomic Layer Deposition, is a technique that has shown promise in depositing these thin films with exceptional precision and control.

E-ALD is a modification of the Atomic Layer Deposition (ALD) technique, which is widely used to deposit thin films of materials for a variety of applications. ALD involves the sequential exposure of a substrate to two or more precursors, each of which reacts with the substrate surface to form a thin layer of the desired material. The key advantage of ALD is its ability to deposit uniform and conformal thin films with precise control over thickness and composition.

E-ALD takes this technique one step further by introducing electrons into the process. The electrons are used to enhance the reactivity of the precursors and promote their adsorption onto the substrate surface. This results in a faster and more efficient deposition process, with fewer defects and higher purity.

One of the primary advantages of E-ALD is its ability to deposit thin films of materials for use in optoelectronic devices. These devices require precise control over the thickness and composition of the thin films to function effectively. For example, solar cells rely on the absorption of photons to generate an electrical current. The thickness of the absorbing layer must be carefully controlled to maximize the absorption of photons and improve the efficiency of the solar cell. E-ALD can provide this precise control over film thickness, allowing for the fabrication of high-performance solar cells.

Similarly, LEDs rely on the precise deposition of thin films of materials to produce light efficiently. The active layer of an LED consists of a thin film of a semiconductor

material that emits light when electrons and holes recombine within the material. The composition and thickness of this layer must be carefully controlled to optimize the efficiency of the LED. E-ALD can provide this precise control over film composition, allowing for the fabrication of high-performance LEDs.

Another advantage of E-ALD is its ability to improve the performance and stability of optoelectronic devices. The precise control over film thickness and composition provided by E-ALD can reduce the number of defects in the thin films and improve their purity. This can lead to improved device performance, such as higher efficiency for solar cells and brighter and longer-lasting LEDs. Additionally, the improved stability of the thin films deposited by E-ALD can increase the lifespan of optoelectronic devices, reducing the need for frequent replacement and improving their overall sustainability.

E-ALD's ability to provide precise control over film thickness and composition, improve device performance and stability, and increase the lifespan of optoelectronic devices makes it an attractive option for researchers and manufacturers in the field. As the demand for high-performance and sustainable optoelectronic devices continues to grow, E-ALD is likely to play an increasingly important role in their fabrication and development.

Microelectronics:

Microelectronics is a branch of electronics that deals with the design, development, and manufacture of electronic components and devices on a microscopic scale. These components and devices are used in a wide range of applications, including computers, smartphones, medical equipment, and automotive systems. The miniaturization of electronic components has led to the development of more powerful and energy-efficient devices that are capable of performing complex functions.

One of the key challenges in microelectronics is the deposition of thin films of materials that are used in the manufacture of various electronic components such as thin-film transistors and capacitors. The deposition of thin films is a critical step in the manufacturing process, as it determines the performance and reliability of the final product. In recent years, a technique known as E-ALD (atomic layer deposition) has emerged as a promising method for depositing thin films of materials in microelectronics.

E-ALD is a thin-film deposition technique that involves the deposition of alternating layers of two or more materials on a substrate. The key advantage of E-ALD is its ability to provide precise control over the thickness and composition of the deposited film. This allows for the creation of thin films with very high uniformity and reproducibility.

The precise control of film thickness and composition provided by E-ALD makes it particularly well-suited for use in microelectronics. In the manufacture of thin-film transistors, for example, E-ALD can be used to deposit thin films of semiconducting materials such as silicon or germanium. These materials are used to create the active layer of the transistor, which is responsible for the control of the flow of electrons in the device. The performance of the transistor is critically dependent on the quality and uniformity of the active layer, and E-ALD can provide the necessary precision and control to achieve high performance and reliability.

In addition to thin-film transistors, E-ALD can also be used to deposit thin films of materials for use in capacitors. Capacitors are passive electronic components that store electrical energy in an electric field. They are used in a wide range of applications, including power supplies, filters, and signal coupling. The performance of capacitors is critically dependent on the dielectric material used in their construction. The dielectric material must have a high dielectric constant (i.e., the ability to store charge) and low leakage current (i.e., the ability to maintain charge). E-ALD can be used to deposit thin films of dielectric materials such as aluminum oxide or hafnium oxide with precisely controlled thickness and composition, which can improve the performance and reliability of capacitors.

Another advantage of E-ALD is its ability to deposit thin films on a wide range of substrates, including silicon, glass, and plastic [15]. This makes it a versatile technique that can be used in a wide range of applications in microelectronics. The ability to deposit thin films on plastic substrates, for example, makes E-ALD well-suited for the manufacture of flexible electronic devices such as displays and sensors. E-ALD is a highly effective process for depositing thin films of materials in microelectronics. Its ability to provide precise control over film thickness and composition makes it particularly well-suited for the manufacture of high-performance and reliable electronic components such as thin-film transistors and capacitors. The versatility of E-ALD, in terms of the range of substrates on which it can deposit thin films, makes it a valuable tool in the development of flexible

electronic devices. EC-ALE can be used to etch a variety of materials, including silicon, III-V semiconductors, and metal oxides, among others. This versatility makes EC-ALE a valuable tool for microelectronics fabrication, where it is important to be able to work with a wide range of materials to create complex structures and devices. Furthermore, EC-ALE can be used to selectively etch different materials, which allows for the creation of complex multi-layered structures, which are increasingly important in the development of modern microelectronics [24], [25].

Cu-Zn is an important semiconductor alloy that has many potential applications in the field of electronics. However, the fabrication of high-quality Cu-Zn thin films is challenging due to the tendency of these materials to form oxides and other unwanted phases during the deposition process. eALD can help overcome these challenges by providing a highly controlled and precise deposition process that minimizes the formation of unwanted phases and produces high-quality thin films with excellent electrical and optical properties [21].

In addition to its precision and control, eALD also offers the ability to deposit a wide range of materials, including complex alloys and composite materials. This makes it an ideal technique for the fabrication of Cu-Zn alloys, which can be tailored to meet the specific needs of different applications. For example, by adjusting the composition of the Cu-Zn alloy, it is possible to control its electrical and optical properties, making it suitable for use in a variety of devices, such as solar cells, light-emitting diodes (LEDs), and transistors.

The use of E-ALD in microelectronics has the potential to drive the development of new and innovative electronic devices that are more powerful, energy-efficient, and sustainable. The precise control of film thickness and composition provided by E-ALD is a key advantage that can improve the performance and reliability of electronic components. The versatility of E-ALD, in terms of the range of substrates on which it can deposit thin films, makes it a valuable tool in the development of flexible electronic devices. As the field of microelectronics continues to evolve, E-ALD will undoubtedly play an increasingly important role in the manufacture of advanced electronic components and devices.

CONCLUSION

E-ALD uses electrochemical reactions to create a layer-by-layer buildup of atoms on a substrate surface. This method provides an unmatched level of control and reproducibility in the deposition of thin films, which makes it an attractive tool for

various applications. E-ALD can be used to deposit a wide range of materials, including metals, semiconductors, and insulators. Moreover, E-ALD enables the deposition of thin films on virtually any substrate, including silicon, glass, and polymers. This versatility has made E-ALD a valuable tool in various fields, including microelectronics, energy storage, catalysis, and sensors.

In the field of microelectronics, E-ALD has become a crucial technique for depositing thin films with precise thickness and composition on semiconductor substrates. The ability to deposit these thin films with such precision has made E-ALD an attractive option for creating advanced microelectronic devices. For example, E-ALD has been used to create high-quality gate oxides in metal-oxide-semiconductor field-effect transistors (MOSFETs), which are essential components of modern microprocessors [26], [27].

Another promising application of E-ALD is in the field of energy storage. E-ALD can be used to create thin films of battery electrode materials with atomic-scale precision, which has the potential to improve the performance and stability of batteries. For example, E-ALD has been used to deposit thin films of lithium cobalt oxide (LiCoO₂) on battery electrodes, which has shown improved capacity retention and cycling stability [28], [29].

Catalysis is another area where E-ALD has shown great potential. The deposition of metal thin films with precise thickness and composition can be used to create catalysts with tunable properties. This allows for the optimization of catalytic activity and selectivity, which is essential for many industrial processes. For example, E-ALD has been used to create platinum thin films with varying thicknesses and compositions, which have shown improved catalytic activity for the oxygen reduction reaction (ORR) in fuel cells.

Sensors are another area where E-ALD has been used extensively. E-ALD enables the creation of thin films with precise thickness and composition, which can be used to create sensors with high sensitivity and selectivity. For example, E-ALD has been used to create gas sensors with high sensitivity and selectivity for detecting gases such as nitrogen dioxide (NO₂) and carbon monoxide (CO).

E-ALD has many advantages over other thin film deposition techniques. One of the most significant benefits of E-ALD is its ability to deposit films with atomic-scale precision. This level of precision is unmatched by other techniques, such as physical

vapor deposition (PVD) or chemical vapor deposition (CVD). Moreover, E-ALD is a self-limiting process, which means that the thickness of the deposited film is determined by the number of cycles and can be precisely controlled.

E-ALD is also a relatively simple process that can be easily scaled up for industrial production. The equipment required for E-ALD is relatively simple, and the process can be carried out in a single chamber, which reduces the need for complex vacuum systems. Additionally, E-ALD is a low-temperature process, which means that it can be used to deposit thin films on temperature-sensitive substrates, such as polymers.

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