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Materials science of thin films

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Thin films are two-dimensional materials created by condensing one-by-one atomic/molecular/ionic species of matter, in contrast to bulk three-dimensional sintered ceramics. The process of fabricating thin films involves the vaporization or sputtering of materials from a source, whereas chemical deposition methods form thin films on solid substrates through chemical reactions. The various techniques used to create these thin films are depicted in Fig. 2. Unlike bulk materials with fixed properties, thin films exhibit unique characteristics due to their reduced thickness. This distinctiveness allows for the creation of devices with specific applications. Thin film devices occupy less space and require fewer materials, making them more cost-effective (Acosta, 2021). The mechanical properties of thin films are heavily influenced by particle size. During fabrication, stresses develop, leading to dislocations that impact hardness and yield strength. As particle size decreases, these parameters increase. The movement of dislocations under stress can strengthen the film. Interactions with microstructural defects like point defects or voids can further enhance this strengthening (Nix, 1989). Reducing particle size increases the mean free path of charge carriers, as they encounter less scattering compared to bulk structures (Gould et al., 2017). However, thin films often contain structural defects such as voids, dangling bonds, and grain boundaries that can trap charge carriers, reducing conductivity (Seto, 1975). The optical response of a thin film with different refractive indices deposited on a glass substrate differs from that of a bulk structure. When visible light is incident on the thin film-glass interface, multiple reflections and transmissions occur at specific angles, unlike in a bulk structure-glass interface. This results in an increase in the extinction coefficient of absorbing thin film layers, modifying optical coefficients (Ignatiev et al., 1979). Thin film deposition involves various chemical reactions, depending on deposition parameters like substrate temperature, rate, pressure, etc. These processes can form amorphous, polycrystalline, or epitaxial thin films. Amorphous films are structures characterized by deviations from a perfect crystal lattice (Pelliccione and Lu, 2008). Low substrate temperatures and high deposition rates can induce amorphous growth. Additionally, the incorporation of gases like oxygen or nitrogen can also form amorphous films (Choy, 2003). Polycrystalline thin films consist of multiple crystalline structures, whereas epitaxial films are highly ordered structures grown on a substrate with a specific crystal structure (joshi et al., 2011). The formation of these different film types depends on the deposition parameters and chemical reactions involved. Thin films are nanoscale materials with thicknesses of less than 1 μm. These ultra-thin structures offer exceptional functional properties that surpass those of bulk materials due to their unique characteristics. Thin film fabrication relies on high-power operating and vacuum conditions, making them crucial for modern technology applications such as magnetic information storage, microelectronics, optical filters, catalysis, and displays. Polycrystalline films form through the coalescence of crystallites that undergo diffusion and nucleation on a solid substrate. Epitaxial thin films, on the other hand, are nearly perfect crystal structures deposited on a substrate with perfectly aligned crystal orientation. Thin films have diverse applications across various fields, including optical, magnetic, electrical, thermal, chemical, and mechanical fields. They can also be used in wearable electronic devices. Fig. 2 illustrates different fabrication methods for thin films. The properties of thin film materials differ significantly from those of bulk materials, making them essential for technological advancements in electronic, electrical, magnetic, and optical devices. Fabrication techniques include physical and chemical methods, which will be discussed later in this study. Ultra-thin films with uniform thickness are promising for future semiconductors and other devices. Atomic layer deposition (ALD) is a suitable technique that offers the above characteristics. ALD has been extensively studied in recent years, with several articles and reviews published on the topic. This review is crucial as micro-semiconductor industries face a critical challenge: further shrinking semiconductor devices. ALD has been found to be an effective solution for addressing this challenge, making it a promising technique for future advancements in thin film technology. ALD stands out due to its self-limiting nature, setting it apart from other physical or chemical deposition methods like electroplating, spin coating, sputtering, PVD, and CVD (Fig. 1b) [6]. While CVD and PVD are widely used in industry, ALD is gaining traction for its unique ability to deposit thin films layer by layer at the nanometer scale thickness [5]. The ALD process involves inserting binary or more reactants (precursors) into a reactor, alternating between precursor pulses and purge gas flow (Fig. 2a and b). ALD differs from CVD in that it requires lower temperatures for precursor decomposition on the substrate surface, allowing for film deposition at a lower temperature [15]. The ALD growth rate is linked to the precursor flux at the substrate surface, making it challenging to determine due to various factors such as temperature, concentration, and pulse time [15]. Despite some similarities with CVD, ALD's self-limiting nature makes it attractive for thin film deposition, particularly in conformal films on complex three-dimensional substrates that cannot be achieved by other techniques [21, 22]. Additionally, ALD is considered an advanced-level deposition process compared to traditional CVD [23]. The ALD process typically involves injecting two precursors alternately with purging inert gases, leading to the growth of a thin film through self-saturation reactions with accessible surface groups, resulting in a self-limiting growth of sub-monolayer films [24]. Thin film technology has gained significant importance in recent years, with applications spanning various fields, including electronics, photovoltaics, data storage, and microwave devices. Thin films can reduce the overall volume of a device while enhancing its properties compared to bulk materials. Atomic layer deposition (ALD) is one such technique that offers several advantages over other thin film deposition methods. This review focuses on highlighting the benefits of ALD in various fields of research, providing insights for upcoming researchers to select the most suitable technique for their study. Table 1 presents various physical and chemical deposition techniques commonly used in thin film technology. The development of new technologies is still evolving to meet the demands of the 21st century. Ferrites are a class of materials with potential applications ranging from millimeter-wave integrated circuits to magnetic recordings, thanks to their extraordinary properties such as high electrical resistivity, low loss characteristics, and strong magnetic coupling at high frequencies. Ferrites exhibit ferromagnetic behavior and have a unique crystal structure, which is crucial for understanding their magnetic properties. The synthesis process plays a significant role in determining the crystallinity and crystal structure of ferrite thin films. References: 1. Tejendra K. Gupta, Ranjeet Kumar Brajpuria (2023). Ferrite Nanostructured Magnetic Materials. 2. [Insert reference 2]. 3. [Insert reference 3]. 4. [Insert reference 4]. Thermal evaporation and epitaxial growth play crucial roles in shaping ferrite spinel crystals. The tetrahedral and octahedral sites within these crystals are essential for their structure. Thin film growth features include initial nucleation, followed by growth phases that rely on parameters like temperature, growth rate, pressure, material chemistry, and substrate structure. Bonding agents can modify the nucleation stage, affecting surface morphology, defect generation, and film stress. The basic properties of thin films involve composition, thickness, microstructure, crystal phase, and orientation, which can be controlled by varying deposition parameters. Thin films exhibit unique features like quantum size effects and strain impact, absent in bulk materials. This chapter focuses on the CVD method for growing ferrite thin films, including types of CVD, growth mechanisms, gas kinetics, precursor requirements, and applications. Thin films are two-dimensional nanostructured materials with layer thickness ranging from fractions of nanometers to micrometers. They form through deposited layers on surfaces obtained by changing states of matter (vapor, solid, liquid, plasma). Condensation of atoms, molecules, and ions occurs, involving the deposition of material in various ways (atom-by-atom, molecule-by-molecule, layer-by-layer). In initial deposition stages, not all substrate surface is homogeneously covered. Atoms initially form clusters or nuclei, filling uncovered spaces with subsequent impinging atoms. This process leads to continuous thin film deposition on the substrate's surface, with specific thickness achieved. Mathematically, an ideal thin film is defined as... Material spreading in two dimensions (x and y) with limited thickness (z), defined as its thickness (t), ranging from t = 0 to arbitrary values, such as 20 μm. The z direction remains less than the other two directions [53]. Factors influencing thin film properties during formation include substrate temperature, deposition rate, material purity, incidence angle, environmental conditions, and energy of depositing particles [54]. Thin film growth involves distinct stages: surface preparation, adatoms and surface diffusion, nucleation, interface formation, and continuous film growth. Surface preparation includes cleaning, altering chemistry, modifying physical properties, developing nucleation sites, and adding reactive agents to enhance the surface. During surface preparation, techniques like diffusion, physical sputtering, chemical reaction, self-assembly, chemical etching, and plasma treatments can be employed. These modifications alter the properties, structure, and texture of thin films. For instance, plasma ions can clean surfaces via physical sputtering [54]. Adatoms interact with the surface at a distance of some Å, losing kinetic energy and momentum to become adsorbed. The jump rate (Γ) of adatom diffusion between sites is influenced by substrate temperature, diffusion barrier (E_d), attempt frequency (ν), and Boltzmann's constant (K_b). The diffusion coefficient (D) is described as $D = 1/4a^2\Gamma$. Nucleation is a primary process during crystal or thin film growth. It involves the formation of islands, coalescence, channel stage, and continuous film growth. The stages differ in terms of adatom and surface interaction mechanisms [56]. Formation from matter takes place through solid, liquid, and vapor forms. Nucleation occurs when small clusters of ions, atoms, or molecules arrange themselves into patterns, providing sites for crystal or thin film growth. This process is characterized by the formation of unstable intermediate structures that eventually give rise to crystalline growth. The nucleation density refers to the amount of surface contact area or voids, which affects the sticking ability of thin films. Factors influencing nucleation density include the kinetic energy of atoms, nucleation sites, chemical reactions, diffusion with the surface, and surface mobility. Interfaces form when two materials meet during the deposition process. They can be classified into various types, including abrupt, mechanical abrupt, diffusion, compound, and pseudodiffusion interfaces. Each interface has distinct electrical, mechanical, and thermal properties that influence its reliability. An abrupt interface is formed through a sudden transition between materials, characterized by a large gradient in material properties and reduced nucleation density. This type of interface results in interfacial voids if nuclei growth is inadequate. On the other hand, a diffusion interface forms when there is interdiffusion between film and substrate materials. While this interface provides good adhesion, it can create voids due to mismatched diffusion rates. Temperature, time, and pressure are essential for atomic diffusion in materials. A compound interface occurs when materials react with each other, resulting in the formation of a new material. This type of interface offers good adhesion but can create voids if there is an imbalance in atom diffusion. When different materials combine, layers of compounds form through chemical, metallurgical, and solid-state reactions. These interfaces may be brittle, but they generally provide good adhesion between materials. However, if voids or microcracks develop, the interface weakens, leading to poor adhesion [54-59]. During the growth process, various phenomena occur. To achieve a positive net growth rate, atoms continuously attach to and detach from grains. Understanding what happens with different-sized grains on the surface without deposition is crucial. In isolated grains, atoms constantly attach and detach, resulting in a size change. A 2D cloud of adatoms surrounds each grain, with larger nuclei exceeding 10 Å [60-61]. The binding energy of surface atoms inversely relates to grain size, while small grains have high adatom density and large grains have low adatom density. When two grains with different sizes interact, the higher-density adatoms flow towards the lower-density adatoms, causing Ostwald ripening [60-61]. As islands grow and eventually meet, they coalesce with gaps. This process forms a grain boundary through the deformation of impinging islands. Coalescence occurs when significant mass transfer happens by diffusion, resulting in the disappearance of small islands. Recrystallization and annealing occur during this process, leading to larger islands with defined shapes [62]. After coalescence, channels and holes form, allowing for continuous deposition. Within these channels, secondary nuclei grow, increasing film thickness and island size. These new islands merge or aggregate by reducing gaps. However, some void spaces may remain, decreasing with increased film thickness. Finally, a continuous thin film forms when all gaps are bridged. Some minor voids might be present, but an ideal film has no gaps. The minimum film thickness depends on the nature of deposits [53]. Properties of a thin film depend on its composition, surface-to-volume ratio, and morphology developed during growth. However, developing thin films with required characteristics in large scale still remains a challenge. A comprehensive understanding of thin film development process and properties is necessary to fully exploit their application potential. This requires precise measurement of thin film parameters during and after production. Among available methods for thin film parameter measurement, nuclear techniques are those that exploit exotic properties of atomic nuclei. Thin films can be just a few atomic layers, measurements based on nuclear techniques where every nucleus participates give better signal-to-noise ratio. Most of these nuclear techniques are non-invasive, very selective, and highly sensitive. We know that thin films are material layers with thickness in the range of nanometres to micrometres. The study of thin film science began from observing metal films formed by high-energy positive ions sputtering the cathode. Since then, it has become a fully-fledged discipline due to its extensive applications in various fields like electronics, optics, defence, aircraft, space science, industries, pharmaceuticals, radar cells, etc. Thin films outperform bulk materials for sensor applications due to better repeatability and high microstructural control. Thin film deposition can be broadly divided into chemical and physical methods. The former includes electrodeposition, sol-gel method, chemical bath deposition, spray pyrolysis, spin coating, etc., while the latter includes sputtering, thermal evaporation, pulsed laser deposition, etc. The superficial morphology of films highly influences their carrier concentration, mobility, photon path length, etc. This review discusses thin film MOS deposited by the chemical spray pyrolysis method for gas sensor applications. In film production processes, three techniques stand out for their effectiveness: Physical Vapor Deposition (PVD), Pulsed Laser Deposition (PLD), and thermal evaporation. These methods cater to diverse applications across industries. ##### Physical Vapor Deposition (PVD) PVD is known for producing thin films and coatings through the deposition of atoms or molecules onto a substrate. 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