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Recent progress in Transparent conducting oxide: Titanium dioxides as material and various processes: A review

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Abstract

This review focuses on the properties and processes of polycrystalline or amorphous Transparent Conducting Oxides (TCO) semiconductors. Among TCO materials, TiO₂ films are considered as important optical films due to their high refractive index, high band gap and transparency over a wide spectral range, adjustable electrical conductivity, perfect chemical stability and environmental nontoxicity. Under ambient conditions, TiO₂ has four known structures: rutile, anatase, brookite, and srilankite. The most stable phase is the rutile structure. As well known, there are a variety of chemical and physical methods were used to obtain TiO₂ thin films with different structures for many applications. There are many research and manufacturing sectors prefer to use the physical vapor deposition techniques in the deposition process of ceramic coatings for multiple applications. Dip coating is a modern CVD process and largely engaged for industrial application due its major advantage of producing high quality film beside the relatively high deposition rate and good adhesion to different metallic and nonmetallic substrates.

titanium compounds, on the other hand, have found limited use in general engineering applications, owing to their poor tribological properties [5]. Because of their enormous physical and chemical properties, titanium compounds such as titanium oxynitrides (TiN_xO_y) are extremely important in a wide range of applications [6]. Because of its excellent combination of chemical and mechanical properties, it is widely used in medicine and the chemical industries [7,8]. Furthermore, titanium

1. Introduction

Transparent conducting oxide (TCO) films have received a lot of attention due to their numerous technological applications, which include solar cells, flat panel displays, light emitting diodes, and gas sensors. Titanium and titanium alloys have several appealing properties, including relatively high specific strength and modulus, good corrosion resistance, and biocompatibility. Therefore, they are widely used in many branches of industries [1-4]. Titanium and

TiO₂ exists in several crystalline forms, including anatase, rutile, and brookite. Many important applications rely on the structure and optical properties of (TiO₂). Solar cell applications benefit from densely structured films, whereas gas sensor applications. Porous films can help you. Rutile phase has good stability and a high refractive index, making it suitable for lens protective coatings. (Takikawa et al., 1999) [15]. The anatase phase, which has better response with ultraviolet photons used for photocatalysis (Yu et al., 2001) [16] whereas amorphous TiO₂ films are utilized in biomedical fields due to its blood compatibility (Liu et al., 2003) [17]. TiO₂ in the form of a thin film is more convenient in photocatalysis than powder because it is very easy to remove from the solution. Furthermore, it has more applications in thin film form, such as coatings on ceramic tiles and self-cleaning windows.

TCO films have received much attention due to their various technological applications in solar cells [18], flat panel displays, touch panels, light-emitting diodes (LEDs), and gas sensors [19]. It is well known that as a wide band gap semiconductor, TiO₂ has a large variety of potential applications and has been extensively investigated [20]. Its excellent performance, as evidenced by its high transparency at visible wavelengths, high refractive index, adjustable electrical conductivity, perfect chemical stability, and environmental nontoxicity [21,22], enables it to act as

nitride (TiN) belongs to the family of refractory transition metal nitrides and has excellent optical, chemical, and physical properties, allowing it to be used in a variety of applications such as hard coating material, hard mask, and diffusion barriers. (S.R. Min et al. 2008) [9]. Nitriding of titanium has been investigated for many years and is used effectively for protection against wear. Nowadays, there is a growing interest in the application titanium compound.

TiO₂ films are important as optical films due to their high refractive index, high band gap and transparency over a wide spectral range, adjustable electrical conductivity, perfect chemical stability and environmental nontoxicity [10,11]. TiO₂ in the thin films form has several properties that make it a material of interest for lots of applications. Indeed, TiO₂ films can be used as a coating in anticorrosive protection, as catalysts in chemical industry and environmental purification phenomena.

TiO₂ depends on its structure and optical properties; rutile phase has good stability and high refractive index [12]. TiO₂ has a wide band gap semiconductor material which has been under extensive investigations due to its applications in a variety of fields such as anti-reflection for solar cells, gas sensor, optical fibers, electrochromic materials for display devices, biomedical fields, etc [13]. It has a combination of good electrical and chemical properties [14].

dipped substrate and the solution are important in the process. Intermolecular forces (hydrogen bonding and Van der Waals forces, for example) that are related to the tendency for liquids to resist separation are affected by cohesive forces. Attractive forces exist between molecules of the same substance and are known as attraction forces. Adhesive forces, on the other hand, are also attractive forces, but between opposing molecules. Other types of forces, such as mechanical and electrostatic forces, are involved in this last case.

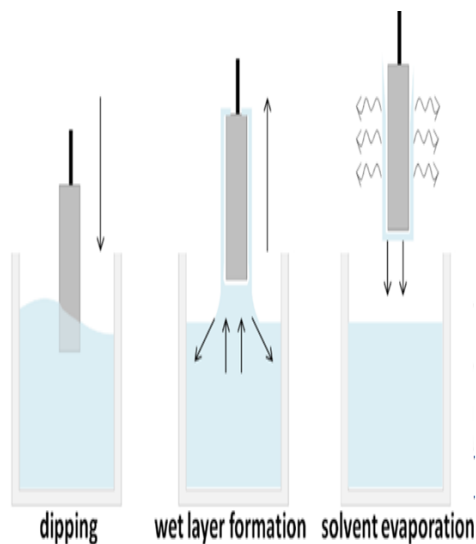


Fig. (1) Dip Coating method.

3. Physical Vapor Deposition (PVD)

The most popular method for creating hard coatings on thin films is physical vapor deposition (PVD). CF Powell et al. first reported this process in a book on vapor deposition in 1966 [34]. PVD tool coatings have been a reality since 1980, and an industry has grown up around them, thanks to the early pioneers' work [35,36]. The sputtering method creates a layer with a higher

an ideal composite layer on some TCO films [23].

It is known that the physical properties of the TiO_2 material strongly depend on the deposition method. TiO_2 films have been prepared by various techniques such as dip coating magnetron sputtering, sol-gel (Fan et al., 2000) [24], pulsed laser deposition (Suda et al., 2005) [25], evaporation (Muaz et al., 2017) [26], chemical vapor deposition (Bergeron et al., 2017) [27], and spray pyrolysis (Oja et al., 2006) [28]. One of them; the physical vapor depositions (PVD) such as cathodic arc deposition, arc ion plating, electron beam evaporation, pulsed laser deposition, magnetron sputtering and vacuum arc evaporation [29,30]. Among the above-mentioned methods Dip coating technique is widely used because of its low processing cost, simplicity, and ability to produce thin and uniform films on large area substrates. Moreover, Dip coating is largely engaged for industrial application due to numerous advantages like high quality film with high deposition and good adhesion to the substrate [31,32].

2. Dip-coating is a technique for making thin films.

The dip-coating process is a popular liquid-phase deposition method for the formation of thin films. This process's technology is based on dipping a substrate into a solution at a controlled rate as shown in Fig. (1). After the liquid component of this solution has dried, the substrate is left with a solid thin film [33]. As a result, the adhesion and cohesive forces between the

either a direct current (DC) or a radio frequency (RF) power supply can produce plasma. Figure 1 depicts the sputtering process in its basic form fig (3). In 1838, Michael Faraday became the first scientist to generate plasma in a vacuum of around 2 Torr. William Robert Grove, who defined the effect as cathode disintegration, was the first to employ this procedure to analyze coatings in 1852. Grove's equipment had a silver-coated copper cathode, but the vacuum he manually pumped was insufficient, therefore the world's first sputter deposited film was most likely silver oxide rather than silver [38].

During deposition, the sputter technique does not require any thermal evaporation of the substrate as shown in fig (2). Sputtering, like any other application, has benefits and drawbacks:

Sputtering's advantages include large-size targets, which ease the deposition of thin films of uniform thickness over large wafers; film thickness can be easily adjusted by modifying the deposition time and establishing the operational parameters.

Sputtering's drawbacks include the need for a large initial investment. Some materials (such as SiO_2) have relatively slow deposition rates. Ionic bombardment can easily destroy some materials, such as organic solids. Ionic bombardment can easily destroy some materials, such as organic solids. Because the former operates at a higher pressure, there is a greater chance of introducing contaminants into the substrate.

density than the evaporation method. The distinction between sputtering and evaporation is caused by the kinetic energy distribution during emission processes[37]. The average kinetic energy distributed by sputtered atoms has a higher peak than that of evaporated atoms, as seen in Fig. (2). The differences between the sputtering and evaporation processes: Produces atoms with a higher energy, It takes place in a plasma path with a low vacuum. a lot of collisions a lot of line-of-sight deposition a lot of gas in the film, produces a grain with a smaller size, There are numerous grain orientations and Results in better adhesion. While evaporation Produces atoms with a lower energy, takes place in a high-vacuum environment with few collisions, line-of-sight deposition, and little gas in the film, Produces larger grain size, There are fewer grain orientations and As a result, adhesion is compromised.

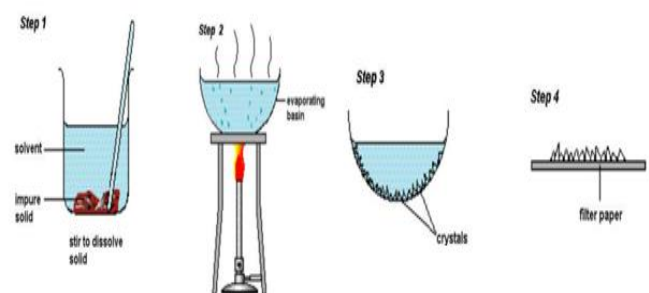


Fig 3 Evaporation method.

4. Sputtering Processes

Sputtering is the bombardment of a target surface with high-energy ions, which causes atoms or molecules of a substance to be expelled. Ionizing an inert gas (such as argon or neon) with

Gerasimov et al. This type of discharge was also investigated in relation to the generation of high-current rotating plasma for nuclear fusion[42]. They also studied an effect of a transverse magnetic field on a glow-discharge mode, [43] plasma instability, [44] and cathode sputtering [45,46]. The presence of a high magnetic field was discovered to improve cathode sputtering.

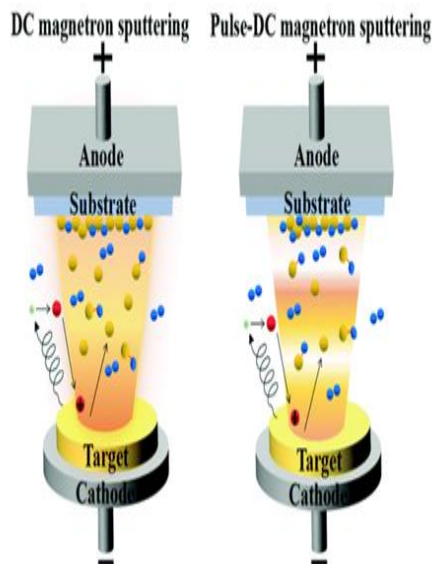


Fig (4) magnetron sputtering
A magnetic field is used in magnetron sputtering to align electron movement into a spiral line, which provides a high ionization density of the argon atoms as well as the possibility of more collisions[47]. The plasma is confined to a small area near the target, causing no damage to the thin film that is being formed. Furthermore, electrons travel a greater distance, increasing the likelihood of further ionizing Argon atoms. This produces a stable plasma with a high ion density. More ions mean more atoms ejected from the target, increasing the efficiency of the sputtering process. The faster ejection

5. Magnetron Sputtering

Penning pioneered low-pressure sputtering by superimposing a transverse magnetic field on a dc glow-discharge tube, as shown in Fig (4) [39]. Magnetron sputtering was reconsidered as an appealing process for thin-film deposition in the early 1960s.

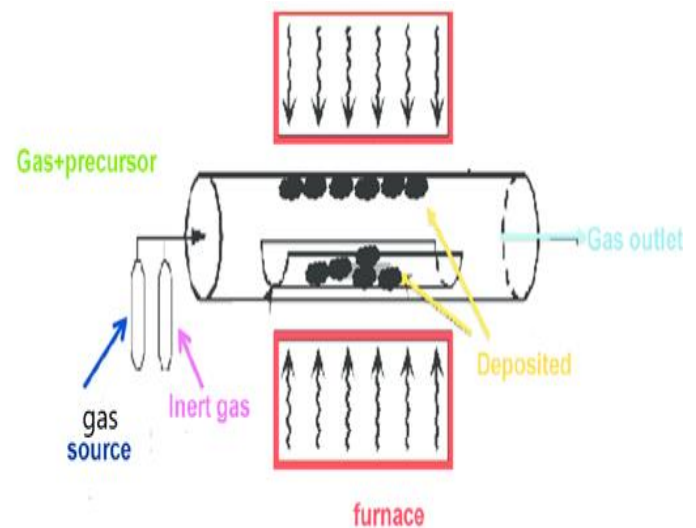


Fig (3) Sputtering method.

[40] The glow discharge in the presence of a magnetic field was investigated in relation to thin-film deposition. He discovered that a quadrupole magnetic field increases ion current density at the cathode by more than one order of magnitude, as well as the rate of deposition. (S. H. Park)[41] suggested an inverted magnetron sputtering system and demonstrated that the sputtering gas pressure may be as low as 10^{-5} Torr, a two-order-of-magnitude reduction over traditional sputtering systems. For the deposition of superconducting thin films, they used an inverted magnetron.

with lower resistivities and optical features superior to those of the current generation[52]. The increasing use of TCO materials, particularly for the fabrication of transparent electrodes for optoelectronic device applications, has resulted in a multibillion-dollar industry that is dependent on ITO availability.

The scarcity and high cost of in endangers this economy. The issue prompts a thorough analysis of the physics and chemistry of Transparent and conductive oxides materials to identify alternatives to ITO. The conductivity of ITO was successfully improved using this principle; Other transparent and conductive oxides, however, have yet to be tested. The attempt to create more mobile Transparent and conductive oxides by using oxides with ns² electron configurations instead of the ns⁰ electron configurations found in standard Transparent and conductive oxides was only partially successful. Despite having the required optical and electrical properties, the conductivity of these wide band gap oxides was limited due to their low band gap. P-type ZnO was created by doping it with N, F, P, Sb, and As. Oxides that are both transparent and conducting; However, it was observed that such doping had significant limitations, and the conductivity was lower than that of n-type ZnO. To recapitulate, the only transparent and conductive oxides with electrical conductivities equivalent to ITO and good optical transmission in the near-UV, VIS, and NIR are AZO, GZO, and

rate, and thus the deposition rate, reduces the formation of impurities in the thin film, and the increased distance between the plasma and the substrate reduces damage caused by stray electrons and argon ions. To address these issues, pulsed magnetron sputtering (PMS) is a new development process. When depositing highly insulating materials, initial experiments have indicated that pulsing the magnetron discharge at medium frequencies (10–200 kHz) can stabilize the discharge, virtually preventing arcing and the creation of defects in the film[48]. Deposition rates for pulsed reactive sputtering are also comparable to those for non-reactive sputtering of pure metal films[49].

6. Transparent Conducting Oxide (TCO)

Transparent and conductive oxide (TCO) layers serve as transparent electrical contacts or electrodes in flat panel displays, touch screens, thin film solar cells, and electrochromic devices, and are essential components for a wide range of photosensitive electronic devices[50,51]. Depending on the application, such metal oxide layers have a wide range of requirements. Transparent conductive electrodes are receiving increased attention for applications in large area photovoltaic devices and displays being developed for energy and electronics. Transparent and conductive oxides (TCO) based on TiO₂, In₂O₃, ZnO, or SnO₂ have been widely employed to date, but advanced technologies require new electrodes

rooms where electronics are assembled. In this application, high surface resistances (e.g., k/cm^2) can be tolerated. Heating elements that are visible TCO coatings can be used to make transparent heating elements. These are used as windshield defrosters in airplanes and automobiles. They have a significant benefit over standard hot air blowers in that they can thaw large areas considerably faster and more uniformly. This application necessitates the use of either extremely low surface resistance coatings (e.g., $1/cm^2$) or a high voltage power source. The application of TCO coatings to passenger vehicles has proven to be technically successful but a commercial failure, due to the high cost of a supplemental alternator to deliver the requisite high voltage. If the automobile industry will adopt a higher bus voltage, as has been widely discussed, then this application may prove to be more commercially feasible in the future.

Solar cells Most solar cells use TCO films as a transparent electrode. Major considerations in the choice of the TCO for this application, besides the conductivity and transparency, are electronic compatibility with adjacent layers in the cell, processing requirements, and stability under environmental conditions. Often tin oxide-based films are chosen for this application, in as much as patterning is not required, but environmental stability is.

FTO. The goal of creating transparent and conductive oxide materials with optical and electrical properties comparable to ITO has yet to be achieved. Shielding can be achieved by using transparent and conductive oxide coatings to reduce electromagnetic radiation interference (EMI) while allowing visual access. This could be done to keep radiation from escaping an enclosure and interfering with neighboring devices or detection, for example. To keep radiation out of an enclosure, preventing external radiation sources from interfering with electronic devices inside. A window in a domestic microwave oven, for example, now has a perforated metal screen to prevent microwave leakage by obscuring clear visual inspection. To avoid harming consumers and interfering with the proliferation of wireless devices that use the unlicensed 2.45 GHz spectral band, radiation leakage must be kept to a minimum. Even though transparent conducting films were proposed 50 years ago, an attempt to market microwave windows with transparent and conductive oxides coatings failed approximately a decade ago due to the expensive cost. Low-cost designs are being created right now.

7. Industrial Application of Transparent and conductive oxides

have a wide range of industrial uses, some of which will be discussed in this section. To minimize dangerous static charge build-up, transparent and conductive oxides coatings are utilised on transparent work surfaces and closet doors, particularly in clean

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8. Conclusion

Understanding the physics of TCO semiconductors has generated the most significant progress in TCO thin film research and development.

The physical processes that allow electrical conductivity and optical transparency to coexist have been thoroughly clarified and comprehended. It is widely known that oxygen vacancies and different dopants play a role in the creation of shallow donor levels. New TCO compounds based on mixed Segre-gated-binaries, ternary, and quaternary oxides have been produced in addition to binary TCOs.

However, the goal of developing new TCOs with conductivities comparable to or even exceeding ITO has not been met. The conductivity of the newly developed ternary, quaternary, and binary-combination TCOs is lower than that of ITO. The negative correlation between carrier density and electron mobility is widely recognized as a barrier to increased conductivity. It is now understood that producing TCOs with higher conductivity does not always necessitate a higher dopant concentration. That results in a higher carrier density but can alternatively be accomplished by keeping a moderate carrier density while increasing mobility. To reduce carrier scattering and promote mobility, conduction electrons and their parents' impurity atoms (ions) should be separated spatially.

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