Research Status of Antireflection Film Based on TiO₂

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Abstract. Solar cells face the disadvantages of high cost, poor reliability and low conversion efficiency. In order to overcome many shortcomings of solar cells and optimize the performance of solar cells, coating anti-reflection film is one of the main optimization methods at present, so it is necessary to prepare anti-reflection film with excellent anti-reflection performance. In this paper, the research results of TiO₂ based anti-reflection films are discussed. The contribution of TiO₂ anti-reflection film to solar cell conversion efficiency is summarized. The preparation methods and processes are discussed.

1. Introduction

1.1. Development history of anti-reflection film

The anti-reflection film has a relatively long history [1], and the earliest anti-reflection was made by J. Frauhofer in 1817 by acid etching. In 1935, the single-layer MgF₂ anti-reflection membrane was prepared and began to be widely used. In 1939, the double-layer anti-reflection film was made. In 1942, the anti-reflection film with excellent wide-spectrum anti-reflection performance was prepared. From 1937 to 1947, the theory of multi-layer film of anti-reflection and anti-reflection coating systems and interference monochromatic filters was successively produced. With the development of science and technology, the performance requirements of anti-reflection coatings are getting higher and higher, and the application fields of anti-reflection films are becoming more and more extensive. In the military, broadband anti-reflection coatings and broadband high-reflection coatings have been widely used in various military optical instruments. In order to improve the photoelectric conversion efficiency, a filter for controlling thermal properties is generally deposited on the cover glass of the solar cell, the filter only allows light transmitted through the visible and near-infrared regions of the sun that can be converted into electrical energy, and harmful infrared radiation will be reflected effectively. At present, optical thin film devices and related preparation technologies have entered the modern high-tech field, the application range of coating components has expanded from traditional optical instruments to...
important fields of national economy such as communication, electronics, biology and medicine. Now, there are many kinds of anti-reflection coatings. The commonly used anti-reflection coatings are SiO2, Si3N4, Ta2O3, etc.

1.2. Preparation process of anti-reflection film

1.2.1. Sol-gel

The sol-gel method was the earliest recorded method for making tofu in the han dynasty of China. It is a method in which an organometallic compound or an inorganic salt is passed through a sol, a gel, and then solidified, and then heat-treated to form an oxide or other solid compound. The advantage of preparing the optical anti-reflection coating by the sol-gel method is that it is convenient to apply multiple coatings, which is advantageous for preparing large-area coating products, and the equipment input cost is small, but the process procedure is complicated, and the film thickness and uniformity control is slightly poor. In 2018, Jung et al. achieved a reflectance of 4.74 in the spectrum of 400 ~ 1000nm by sol-gel Al2O3/TiO2 double-layer anti-reflection film [2].

1.2.2. Magnetron sputtering

Magnetron sputtering is a common thin film deposition method with good reproducibility, especially in microelectronics and material surface treatment for thin film deposition and Cover layer preparation. Magnetron sputtering has a wide range of applications, and easy control of components [3], but it also has some shortcomings such as target. The utilization rate of the material is low, the sputtering power is large, the equipment is complicated, and the production cost is high. In 2017, Niakov et al. used high-pulse power magnetron sputtering (HiPIMS) to deposit TiO2 thin films on the tissue surface. The TiO2 antireflection film has the advantages of flat surface, relatively low reflectivity and high refractive index [4].

1.2.3. Ion beam sputtering coating technology

Ion beam sputtering technology usually uses a argon ion beam obtained by ionization, acceleration and focusing in an ion source to bombard the surface of the target at a certain angle to cause cascade collision of the target atoms and a large number of atomic detachment. The surface of the target becomes sputtered particles and is deposited directly onto the substrate to form a thin film. Generally, the coating used for anti-reflection is mostly a dielectric material such as an oxide or a nitride, and is usually plated by reactive sputtering deposition. It is difficult to strictly maintain the stoichiometric ratio, and it is easy to cause problems such as excessive absorption of the coating. And compared with other coating processes, the film formation rate of ion beam sputtering is slower, so the process time is longer. In 2018, Nancy Sharma et al. used electron beam deposition technology to design and deposit a single layer with a reflectivity of 96.41% and a multi-layer anti-reflection coating with a reflectivity of 94.09% on a glass substrate [5].

1.2.4. Vacuum evaporation coating

Compared with other film forming methods, vacuum evaporation has the advantages of simple process, easy operation, high film formation speed and high efficiency, so it is widely used for plating of anti-reflection film. The development of vacuum evaporation is mainly reflected in the way of heating and evaporating materials. According to the different heating methods, it can be divided into resistance heating and electron beam heating. Resistance heating has been around for nearly a hundred years. This method can not evaporate the high melting point material due to the limited temperature, and the material is easily chemically reacted with the evaporator at a high temperature, so that only a part of
the material can be plated. Electron beam heating is a relatively common preparation method in the preparation of optical films. It can increase the density and stoichiometric ratio of the film and improve the adhesion of the film layer, thus facilitating the preparation of optical films with stable performance. In 2013, Fu Rui et al. optimized the design of 350nm-1800nm wide-band anti-reflection film by TFC film design software. Based on this, the TiO$_2$/SiO$_2$ double-layer anti-reflection coating was prepared by electron beam evaporation. It has a good anti-reflection effect in the 400-1000 nm band, with an average reflectance of 4.87% and a minimum reflectance near the wavelengths of 450 nm and 800 nm$^6$.

2. Research progress of TiO$_2$ optical anti-reflection film

TiO$_2$ coating is an optical film that is highly transparent to visible light and near-infrared light and strongly absorbs ultraviolet light. Its transparent band is 0.36um$-9$um, its refractive index is high, and it can be chemically and mechanically stable with the change of preparation process. It has good space-resistant radiation characteristics and has become one of the most widely used anti-reflection coatings. It has an irreplaceable advantage in the new graded refractive index film structure. In addition, TiO$_2$ coating also has good photocatalytic and photoinduced hydrophilicity $^7$, which can effectively achieve self-cleaning and sterilizing functions. Therefore, TiO$_2$ coating is a promising functional film, which is combined with other. The optical film materials are matched together, and the anti-reflection coating system can be realized by rational design and construction, which not only can achieve better optical performance, but also improve the self-cleaning function of the film. This is of great significance for improving the light efficiency and service life of optical devices. TiO$_2$ coating is an optical film that is highly transparent to visible light and near-infrared light and strongly absorbs ultraviolet light. The transparent band is 0.36um-9um, the refractive index is higher and can change with the preparation process. There are three different structures about titanium dioxide. Anatase, brookite, rutile. Anatase and rutile have better anti-reflection properties. These two crystal structures are shown in Figure 1.

![Figure 1. Crystal structure of rutile and anatase titanium dioxide](image)

2.1. Preparation of single-layer TiO$_2$ anti-reflection film

According to the optical anti-reflection principle, it is not suitable for the high refractive index TiO$_2$ material to be used as single anti-reflection coating alone, and it is usually combined with other low-refractive-index film designs to form a double layer, a triple layer, and the multi-layer TiO$_2$ optical anti-reflection coating, so that the system can fully reflect its excellent optical properties. But in 2018, Tsung-chengchen et al. applied the single material TiO$_2$ film to the anti-reflection and surface passivation of p-type c-si by atomic layer deposition. Here we showed that both functions can be
satisfied by single material of titanium oxide film through atomic layer deposition at low temperatures.[8]

2.2. Preparation of double-layer TiO₂ anti-reflection film

In 2009, Omer Kesmez et al. prepared SiO₂/TiO₂ bilayer films by sol-gel method, which not only has the effect of anti-reflection but also has the function of self-cleaning[9], it’s structure shows in Figure 2.

![Figure 2. Silicon-based SiO₂/TiO₂ double-layer anti-reflection film structure](image)

In 2017, Suma Hikmet al-shaikh Hussin et al. prepared nano porous titanium dioxide films doped with Er and La films by sol-gel method. The results show that the nanofilm (2 Layers SiO₂-4 Layers (TiO₂+0.02Er) have the highest transmittance which shift the spectrum about Δλ=64 nm towards visible region. In 2017, Binbin Jin et al. proposed a reasonable and well-organized macroscopic mesoporous nanostructure design and construction on the basis of effective medium theory and time-domain finite difference simulation combined with optical design principle, so as to obtain high-performance self-cleaning anti-reflection film[10]. The effective reflectivity of SiOₓ/TiO₂ for silicon solar cell double-layer anti-reflection film designed by Wan Gang and Ye Dejun et al. was about 5%. the short-circuit current gain of the battery is 45%, and the conversion efficiency gain is 47% [11]. The Al₂O₃/TiO₂ double-layer anti-reflection film coated by Hanying Liu et al. on the silicon substrate increases the short-circuit current of solar cells by about 48%[12]. With the continuous improvement of the performance requirements of optical devices, wide-band and high-efficiency anti-reflection has become the pursuit goal of many photovoltaic devices, which requires a more reasonable anti-reflection film system structure, and stable and high refractive index TiO₂ has become one of the most commonly used film materials. For example, Tan Yu, Liang Hongjun and others used TiO₂, SiO₂ and MgF₂ materials to successfully design and prepare 8 0.4um~1.1um ultra-wideband anti-reflection coating on the surface of K9 glass[13], and the residual reflectance at each wavelength position is low, about 1%. At the same time, in recent years, the graded index anti-reflection coating with broadband and all-round anti-reflection characteristics has been paid more and more attention by film workers all of the world. TiO₂ has begun to perform in the graded film structure due to its high refractive index and flexible control. Out of its unique advantages, Shi Beibei et al. studied the SiO₂-TiO₂ chemical composition mixed structure film by sol-gel method [14], prepared single layer and double on the surface of the single crystal silicon substrate. The layer and the three-layer anti-reflection coating have better anti-reflection effects. However, the research on this graded-index anti-reflection film is still rare, so it still has great research value.
2.3. Preparation of multi-layer TiO₂ anti-reflection Coating

Shu-Yang Lien et al. used a spin coating method to coat a silicon solar cell with a certain thickness of single layer TiO₂, two layers of SiO₂/TiO₂, and three layers of SiO₂/SiO₂-TiO₂/TiO₂ antireflection coating. The reflectance of the three films in the range of 400-1000 nm is 9.3%, 6.2% and 3.2%, respectively. The best performance anti-reflection coating improves the anti-reflection performance by 39% in practical applications. In addition, the film system of many materials is not usually superior to the two materials[15]. Zheng Zhenrong et al. successfully prepared a vertical incident ultra-wideband anti-reflection coating by electron beam evaporation using TiO₂ and MgF₂ materials. The average residual reflectance in the 520 nm range is about 0.44%, which indicates that the design of the ultra-wideband anti-reflection coating with two materials is successful and is superior to the anti-reflection film prepared by various materials under certain conditions[16]. In 2018, Ryosuke WATANABE et al. prepared a three-layer optimized anti-reflection coating with a reflectivity lower than 0.048 at the wavelength of 600 nm by wet method[17].

3. Summary and outlook

TiO₂ minus reflection film system as a kind of widely used minus reflection membrane, its preparation method is numerous, has good application prospect, but in the roasting annealing microtek easy in anatase type, plate titanium ore, rutile transformation that occurs in three kinds of crystal to the transformation of the experimental accuracy is not easy to be mastered, the board type titanium mineral crystal does not have as minus reflection membrane characteristics, affect the performance of TiO₂ minus reflection film. In addition, although TiO₂ film can be combined with a variety of materials to form a double-layer film or a multi-layer film, the performance of its single-layer anti-reflection film has been further explored and optimized. With the application of various non-traditional technologies in the preparation of anti-reflection membrane, TiO₂ is being further explored in the preparation of TiO₂ by various non-traditional technologies. Due to the application of TiO₂ in photocatalysis and self-cleaning, the development of TiO₂ anti-reflection film is moving towards the trend of composite multi-function.

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