Sample Translation

Materials Engineering

- See below for the original Chinese manuscript.
- **A native-speaker of English who has studied this field** proofreads the translated English.
- The quality of the translated manuscript is suitable for publication in an international journal.

Growth Behavior and Microstructure of Arc Ion Plated Titanium Dioxide

Abstract

Titanium dioxide (TiO_2) film prepared by Physical Vapor Deposition (PVD) has been developed and extensively applied due to its self-cleaning, photocatalytic, and antimicrobial characteristics. However, many questions concerning its growth processes and microstructures remain unsolved. The present study has employed PVD arc ion plating (AIP) to deposit TiO_2 film to study its growth behavior through microstructural investigation.

According to the thermodynamic calculation, the free energy of the rutile phase is lower than that of the anatase. Theoretically, rutile instead of anatase will grow under any deposition condition. Previous results, however, indicate that the TiO_2 film obtained in oxygen-deficient environment shows a microstructure of amorphous matrix mixed with rutile crystallites. On the other hand, under oxygen-rich conditions, the initial phase formed is rutile, consistent with the thermodynamic calculation, and the anatase phase emergence in later stages is a kinetics problem. Furthermore, the plasma is detected by optical emission spectroscopy (OES) and it is confirmed that with increasing oxygen pressure or deposition time, the extent of target surface oxidation and neutral titanium atom content increases. Consequently, only the activation energy corresponding to the metastable anatase phase can be overcome, and thus only the metastable anatase phase can grow. Finally, the growth mechanism of AIP-TiO_2 can provide a selection base of deposition parameters for the immobilization technology of photocatalytic thin films.

Keywords: Arc ion plating (AIP); optical emission spectroscopy (OES); titanium dioxide; Amorphous; crystallite; Rutile; Anatase

1. Introduction

With its sustainable, self-cleaning, photocatalytic, and antimicrobial characteristics, TiO_2 has been extensively developed and applied in various fields. Immobilization has become a key in widening its application. Using an appropriate deposition process to prepare TiO_2 film with photocatalytic anatase as its target phase to achieve immobilization and thus attain sustainability has been a common goal for many researchers. Many TiO_2 deposition processes have been developed, including sol-gel processes with a wetting approach [2–4], chemical vapor deposition (CVD) [5, 6] processes, and various physical vapor deposition (PVD) processes, such as sputter deposition [7–9], ion beam assisted deposition (IBAD) [10], and arc ion plating (AIP)[11–14]. Distinct phases, including rutile (R) and anatase (A), were reported and formed under different growth conditions. Rutile is the target phase for white pigment and optical devices, whereas anatase is the necessary phase structure for the photocatalytic applications such as antimicrobial deodorizers [16,17], decomposition of organic substances in water [18], handling heavy metallic ions [19], and purification of exhaust gases [20,21].

Among the processes described above, PVD with clean and pollution-free characteristics have received much attention. Film structure is closely related to operating pressure, substrate temperature, substrate bias, and oxygen partial pressure. It has been pointed out that an amorphous structure, rutile phase, and anatase phase may form during PVD processes. The phase structure obtained is largely determined by ion energy and temperature [12, 13]. Zhang et al. [14] indicated that, under a fixed heating source and no substrate bias, TiO_2 film was an amorphous structure; however, when substrate bias was applied, rutile phase was observed. Clearly, substrate temperature and substrate bias played important roles in determining the film structure. Amorphous phases may transform into high-temperature stable rutile, without going through the anatase phase. On the other hand, Zeman et al. [22], concluded that the total pressure and oxygen partial pressure are important parameters for deposition rate, phase composition, crystallinity, and surface morphology. However, the reason why the rutile phase came before the anatase remains unexplained. Ma et al. [23] considered that a high-energy laser beam emitted by an infrared femtosecond laser can partially transform the stable rutile phase into the anatase phase. The extreme high heating and cooling rate provided by the laser was apparently responsible for non-equilibrium phase transformation.

Arc-ion plating has been shown to possess the advantages of high ionization, low temperature deposition, high growth rate, and strong film adhesion. Furthermore, the authors' previous experiments have concluded the antimicrobial effect of photocatalytic TiO_2 film is present [24–26]. Consequently, the present study aims to investigate the film microstructure and to elucidate the growth mechanism of AIP-TiO_2 film.

Abstract

具有自洁、光触媒和抗菌作用的物理气相沉积(Physical vapor deposition, PVD)二氧化钛(TiO_2)镀膜已经被广泛地发展与应用，然而对其生长过程及微观结构仍然有许多地方未研究透彻。本研究采用物理气相沉积法电弧离子镀(Arc ion plating, AIP)被覆 TiO_2 镀膜，通过材料微观分析来了解镀膜的生长行为。

由热力学计算得知：金红石相的生长自由能低于锐钛矿相，理论上在任何施镀条件下应生长金红石相。但研究结果显示：缺氧条件下所得到的 TiO_2 镀膜在 TEM 下呈现出非晶母体夹杂金红石微晶的结构，富氧的条件下初始生成金红石相，满足热力学计算结果，后期生成的锐钛矿相则与动力学有关。经光学发射光谱法(Optical emission spectroscopy, OES)证实有等离子体存在；随着氧气分压或沉积时间增加，因靶面氧化程度增加，零价的中性钛原子增多，由于仅能克服较低生长活化能的锐钛矿相，因而生长出亚稳态(Metastable)锐钛矿相结构。通过对 AIP-TiO_2 镀膜生长机理的了解，为光触媒薄膜的固定化技术提供重要的施镀参数选择依据。

Keywords: Arc ion plating (AIP); optical emission spectroscopy (OES); titanium dioxide; Amorphous; crystallite; Rutile; Anatase

1. Introduction

具有可持续性、自洁、光触媒和抗菌作用的二氧化钛(TiO_2)已经被广泛地发展与应用，如何将其固定化(Immobilization)[1]是应用推广的重要关键技术。以适当的镀膜过程来制备具有锐钛矿光触媒目标相结构的 TiO_2，使其在应用环境中能牢固而不受损耗，从而发挥它的可持续性成为镀膜研究人员追求的目标。先后有许多制备 TiO_2 镀膜的方法，例如湿式制程的溶胶凝胶法(Sol-gel process)[2–4]、化学气相沉积法(Chemical vapor deposition, CVD)[5,6]以及物理气相沉积法(Physical vapour deposition, PVD)中的许多方法，如溅射沉积法(Sputter deposition)[7–9]、离子束辅助沉积法(Ion beam assisted deposition, IBAD)[10]、以及电弧离子镀法(Arc ion plating, AIP)[11–14]等。也先后报导了不同生长条件下对应的不同相结构，包括金红石相(Rutile, R)以及锐钛矿相(Anatase, A)，前者是白色涂料及光学组件上的目标相结构[15]，而后者则是抗菌除臭[16,17]、分解水中有机物[18]、处理重金属离子[19]、废气净化[20,21]等光触媒应用的必要相结构。

上述诸多制程中，着眼于洁净、无公害的 PVD 制程较受瞩目。镀膜结构与工作压力、基材温度、基材偏压及氧气分压十分相关。研究人员指出在 PVD 镀膜过程中，可制备出非晶、金红石相及锐钛矿相。相结构的生成取决于离子能量(Ion energy)以及温度[12,13]。Zhang 等人的研究[14]指出，在有固定热源及没有基材偏压的条件下，TiO_2 镀膜呈现非晶(Amorphous)结构，施以基材偏压则会生成金红石相结构，显然基材温度及基材偏压在镀膜结构的改变上扮演着重要角色，因此有可能在固定热源的条件下由非晶相直接转变成高温稳定的金红石相，而不用经过锐钛矿相。而 Zeman 等人的研究[22]指出，沉积操作总压(Operating total pressure)与氧气分压是控制沉积速率(Deposition rate)、相组成(Phase composition)、结晶性(Crystallinity)与表面形貌(Surface morphology)的重要参数。但仍未明确指出金红石相结构优先于锐钛矿相生成的原因。而 Ma 等人的研究[23]指出，由近红外飞秒激光法(Infrared femtosecond laser)所发出的高能量激光可将稳定的金红石相结构局部转变为锐钛矿相结构，显然是由激光所产生的快速加热与冷却所造成的非平衡相变化导致的。

着眼于电弧离子镀技术在高离化率、低温沉积、高生长速率及镀膜附着性强的优势，并且在先前一系列探讨中也证实了光触媒 TiO_2 镀膜的抗菌效能[24–26]，所以针对镀膜微观组织加以探讨，以充分了解 AIP-TiO_2 镀膜的生长机制。