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

具有自潔、光觸媒和抗菌作用的物理氣相沉積(Physical vapor deposition, PVD)二氧化鈦(TiO_2)鍍膜已被廣泛發展與應用，然對其生長過程及微觀結構仍有諸多必須釐清之處。本研究採用物理氣相沉積法之電弧離子鍍(Arc ion plating, AIP)被覆 TiO_2 鍍膜，透過材料微觀分析來了解鍍膜的成長行爲。

從熱力學計算得知；金紅石相生長自由能低於銳鈦礦相，理論上在任何施鍍條件下應生長金紅石相，但研究結果顯示：缺氧條件所得之 TiO_2 鍍膜在 TEM 下呈現出非晶母體夾雜金紅石微晶之結構，富氧的條件下初始成長爲金紅石相，滿足熱力學計算結果，後期生成的銳鈦礦相則與動力學有關。經光放射光譜法(Optical emission spectroscopy, OES)偵測電漿後證實；隨著氧氣分壓或沉積時間增加，因靶面氧化程度增加，零價之中性鈦原子含量提高，因此僅能克服較低生長活化能之銳鈦礦相，因而發展出介穩態(Metastable)銳鈦礦相結構。透過此一 AIP-TiO_2 鍍膜生長機制的了解，爲光觸媒薄膜的固定化技術提供重要的施鍍參數選擇依據。

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

1. Introduction

具有永效性、自潔、光觸媒和抗菌作用的二氧化鈦(TiO_2)已被廣泛發展與應用，將其固定化(Immobilization)[1]是應用推廣的重要關鍵技術。以適當的鍍膜製程來製備具有銳鈦礦光觸媒目標相結構之 TiO_2，使其在使用環境中能牢固而不流失從而發揮它的永效性成爲鍍膜研究人員追求之目標。因而先後發展出許多製備 TiO_2 鍍膜的方法，如濕式製程的溶膠凝膠法(Sol-gel process)[2–4]、化學氣相沉積法(Chemical vapor deposition, CVD)[5,6]以及物理氣相沉積法(Physical vapour deposition, PVD)中之諸多方法，如濺鍍法(Sputter deposition)[7–9]、離子束輔助沉積法(Ion beam assisted deposition, IBAD)[10]、及電弧離子鍍法(Arc ion plating, AIP)[11–14]等。先後也報導出不同生長條件下對應出不同的相結構，包括金紅石相(Rutile, R)及銳鈦礦相(Anatase, A)，前者是白色塗料及光學元件上的目標相結構[15]，而後者則是抗菌除臭[16,17]、分解水中有機物[18]、處理重金屬離子[19]、廢氣淨化[20,21]等光觸媒應用之必要相結構。

上述諸多製程中，著眼於潔淨、無公害之 PVD 製程較受矚目。鍍膜結構與工作壓力、基材溫度、基材偏壓及氧氣分壓息息相關。研究人員指出在 PVD 鍍膜製程中，可製備出非晶、金紅石相及銳鈦礦相。相結構的生成取決於離子能量(Ion energy)及溫度[12,13]。Zhang 等人的研究[14]指出，在有固定熱源及沒有基材偏壓的條件下，TiO_2 鍍膜呈現非晶(Amorphous)結構，施以基材偏壓則會生成金紅石相結構，顯然基材溫度及基材偏壓在鍍膜結構的改變上扮演重要角色角色，因此有可能在固定熱源的條件中由非晶質相直接轉變成高溫穩定的金紅石相，而不用經過銳鈦礦相。而 Zeman 等人的研究[22]指出，沉積總壓(Operating total pressure)與氧氣分壓是控制沉積速率(Deposition rate)、相組成(Phase composition)、結晶性(Crystallinity)與表面形貌(Surface morphology)的重要參數。但仍無明確指出金紅石相結構優先銳鈦礦相生成的原因。而 Ma 等人的研究[23]指出，藉由近紅外線飛秒雷射法(Infrared femtosecond laser)所施予之雷射高能量可將穩定之金紅石相結構局部轉爲銳鈦礦相結構，顯然是施以雷射所產生之極速加熱與冷卻所造成的非平衡相變化所致。

著眼於電弧離子鍍技術在高離化率、低溫沉積、高成長速率及鍍膜附著性強的優勢，且在先前系列探討中亦證實了光觸媒 TiO_2 鍍膜的抗菌效能[24–26]，遂針對鍍膜微觀組織做探討，藉以釐清 AIP-TiO_2 鍍膜的成長機制。