Surface & Coatings Technology 205 (2010) 1611–1617

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Study of bactericidal efficiency of magnetron sputtered TiO_2 films deposited at varying oxygen partial pressure

A.B. Panda [a], P. Laha [a], K. Harish [a], B. Sarkar [b], S.V. Chaure [c], W.A. Sayyad [c], V.S. Jadhav [c], G.R. Kulkarni [c], D. Sasmal [b], P.K. Barhai [a], A.K. Das [d], S.K. Mahapatra [a], I. Banerjee [a,*]

[a] Department of Applied Physics, Birla Institute of Technology, Mesra, Ranchi 835215, India
[b] Department of Pharmaceutical Sciences, Birla Institute of Technology, Mesra, Ranchi 835215, India
[c] Department of Physics, University of Pune, Pune 7, India
[d] Laser and Plasma Technology Division, Bhabha Atomic Research Center, Mumbai 400085, India

ARTICLE INFO

Available online 4 August 2010

Keywords:
TiO_2 films
Oxygen partial pressure
XPS
TEM
SEM
Bactericidal efficiency

ABSTRACT

TiO_2 thin films have been deposited at different Ar:O_2 gas ratios (20:80,70:30,50:50,and 40:60 in sccm) by rf reactive magnetron sputtering at a constant power of 200 W. The formation of TiO_2 was confirmed by X-ray photoelectron spectroscopy (XPS). The oxygen percentage in the films was found to increase with an increase in oxygen partial pressure during deposition. The oxygen content in the film was estimated from XPS measurement. Band gap of the films was calculated from the UV–Visible transmittance spectra. Increase in oxygen content in the films showed substantial increase in optical band gap from 2.8 eV to 3.78 eV. The Ar:O_2 gas ratio was found to affect the particle size of the films determined by a transmission electron microscope (TEM). The particle size was found to be varying between 10 and 25 nm. The bactericidal efficiency of the deposited films was investigated using *Escherichia coli* (*E. coli*) cells under 1 h UV irradiation. The growth of *E. coli* cells was estimated through the Optical Density measurement by UV–Visible absorbance spectra. The qualitative analysis of the bactericidal efficiency of the deposited films after UV irradiation was observed through SEM. A correlation between the optical band gap, particle size and bactericidal efficiency of the TiO_2 films at different argon:oxygen gas ratio has been studied.

1. Introduction

The rapid growth of a broad range of pathogens like bacteria, protozoan and viruses in water causes various diseases in the human body. Therefore, TiO_2 which is a biocompatible material having a large optical band gap has been employed for purification of water since the discovery of photo-induced decomposition of water on TiO_2 electrodes by Fujishima and Honda in 1971 [1]. When ultraviolet light of energy greater than the band gap of TiO_2 is incident on it, highly reducing electrons are generated in the conduction band and oxidizing holes are generated in the valence band. These under aqueous condition, form highly reactive species such as OH•, O_2^-, HO_2•, and H_2O_2,which are capable of destroying chemical and biological contaminants of water [2,3]. Photocatalytic reaction using TiO_2 powder materials was reported by Matsunga et al. [4] in 1985. Reports are available on water purification using TiO_2 in powder form, which is practically difficult for daily use along with cost effectiveness [5–8]. Whereas, such applications using TiO_2 in the form of thin film is a better alternative on account of its durability, stability and feasibility. Therefore, it is necessary to produce good quality of TiO_2 thin films with desired enhancement of bactericidal efficiency. Out of several techniques, rf reactive magnetron sputtering process is preferentially used for the preparation of TiO_2 thin films. The technique provides large area uniformity of film thickness and strong adhesion to substrate. However, the nature and properties of the film depend on the deposition conditions [9,10]. Researchers have focused their attention on the bactericidal efficiency of TiO_2 crystalline films especially anatase structure and a very few articles are available on the amorphous films [11–13]. Although it has been well documented [14] that the amorphous contents in a product of TiO_2 lowers its photocatalytic activity, however, amorphous TiO_2 films of confined size and higher energy band gap can efficiently undergo photocatalysis [11–13]. Photo killing of bacteria strongly depends on the microstructure i.e., particle size, band gap, film thickness, and hydrophilicity of the deposited films. These properties of the films can be controlled through the deposition parameters like substrate to target distance, substrate bias, sputtering and reactive gas ratios etc. The ratio of Ar:O_2 gases is one of the important factors playing a key role in controlling the physical parameters of the deposited films [15,16]. Hence, one attempt has been made to establish a correlation between bactericidal efficiency and the physical properties of the procured TiO_2 films deposited at different Ar:O_2 gas ratios.

* Corresponding author.
E-mail address: indranibanerjee@bitmesra.ac.in (I. Banerjee).

0257-8972/$ – see front matter
doi:10.1016/j.surfcoat.2010.07.101

In this paper, TiO_2 thin films have been deposited at different oxygen flow rates keeping constant rf power and working pressure by adjusting the Ar and oxygen flow rate to the chamber during deposition. The bactericidal efficiency has been investigated with prepared TiO_2 thin film using UV irradiation. The films have been characterized by X-ray diffractometer (XRD), X-ray photoelectron spectra (XPS), transmission electron microscope (TEM) and UV–Vis techniques. The quantitative analysis of the cell damage and the number of dead bacteria cells was estimated by optical density (OD) measurement whereas, the qualitative analysis was done using scanning electron microscope (SEM) images of the cells. For observation, the bacteria cells were drop coated on a clean sterilized silicon (10 mm × 10 mm) substrates. The samples were then visualized under a scanning electron microscope (SEM).

2. Experimental details

2.1. Deposition of TiO_2 thin films

Titanium oxide films were prepared using rf magnetron sputtering system (MSC-3, JE Plasma Consult GmbH). The titanium vapour produced by sputtering reacts with oxygen species on the substrate surface to form oxide compounds during growth. The vapour of the compounds formed gets deposited atom by atom on the substrate through heterogeneous nucleation. The film growth process is driven by the solid–vapour transformation through the heat released to the substrate [17,18]. There are certain factors that govern the deposition. At low reactive gas flow, the reactive gas is almost completely reacted with sputtered Ti and hence the target condition remains metallic. Further addition of the reactive gas results not only in the formation of a compound on the substrate but also on the target or cathode surface. This can result in a sudden decrease of the deposition rate and an abrupt change in the partial pressure of the reactive gas, the so-called hysteresis or poisoning effect [19,20]. However, a too low supply of the reactive gas may give rise to an understoichiometric composition of deposited films whereas high supply of reactive gas may reduce the deposition rate due to target poisoning [19,20]. Hence for desired deposition of the oxide films, the controlled flow of the reactive and sputtered gas has to be maintained.

A schematic diagram of the deposition system is shown in Fig. 1. The system consists of a chamber coupled with diffusion and rotary vacuum system, planar unbalanced magnetron, pure Ti (99.99%) sputter target (3″ diameter, 3 mm thickness) and rf source of 13.56 MHz frequency. As it is desired to deposit titanium oxides, argon and oxygen are used as the main sputtering and reactive gas respectively. In order to maintain a constant total pressure or working pressure during deposition in the chamber, the flow rate of Ar and oxygen is controlled through MKS mass flow controllers (range 100 sccm) keeping the total pressure constant during deposition i.e. when magnetron was on. The films were deposited on the glass and quartz substrates mounted on a movable (150 mm) and rotatable (360°) substrate holder placed above the magnetron sputter sources attached to the inner roof of the vacuum chamber. The substrates were ultrasonicated by acetone prior to deposition. During deposition, the parameters fixed were, target–substrate distance at 60 mm, rf power at 200 W, working pressure at 10^{-2} mbar and the deposition time of 1 h. The deposition was done under room temperature and without substrate bias for heating. Under this condition, series of four

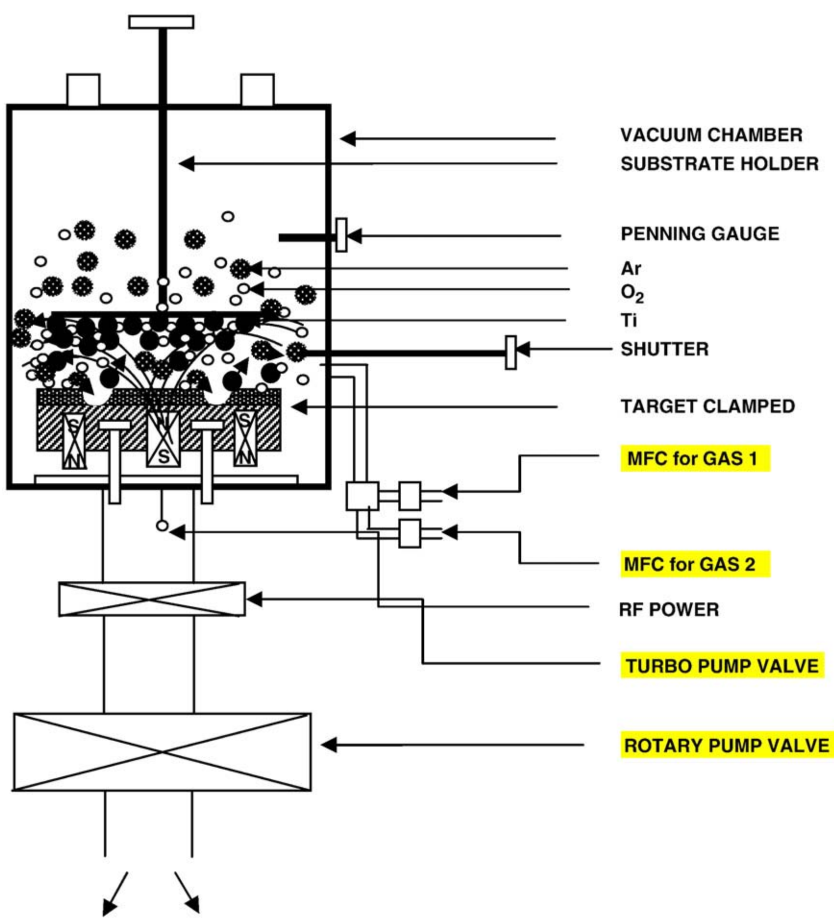

Fig. 1. The schematic diagram of the TiO_2 deposition unit depicting the deposition concept.