EFFECTS OF SUBSTRATES ON THE PHOTOELECTROCHEMICAL PROPERTIES OF TIO_2 THIN FILMS GROWN BY ATOMIC LAYER DEPOSITION

Chia-Chuan Chen[a,*] , Yu-Hung Hsieh[b] , Hsyi-En Cheng[a,b]

[a] Institute of Nanotechnology, Southern Taiwan University, Tainan, TAIWAN
[b]Department of Electro-Optical engineering, Southern Taiwan University, Tainan, TAIWAN
*E-mail: M95R0214@webmail.stut.edu.tw

Abstract

In this study TiO_2 thin films were grown on several substrates at 400 °C by atomic layer deposition from $TiCl_4$ and H_2O precursors. The film properties were characterized by XRD patterns, SEM images and photoresponse currents. The results show that the TiO_2 films grown on Ta substrates possesss a higher photocurrent than those on other substrates. The photocurrents are 70 、60 、30 and 11 μA/cm^2 for Ta, Ti, Ni and Si substrates, respectively.

Introduction

Since the photoinduced decomposition of water on TiO_2 electrodes was discovered, there has been a tremendous amount of scientific interest on the subject [1]. Among various semiconductors, TiO_2 has proven to be the most suitable for environment applications and has been widely employed to photocatalytic degradation of harmful organic compounds [2]. Atomic layer deposition (ALD) is a gas-phase thin film deposition method based on alternate saturative surface reactions [3,4]. The precursor vapours are pulsed into the reactor once at a time and separated by purging with an inert gas. During each precursor pulse, the surface becomes saturated with the precursor, which results in a self-limited film growth. The self-limited films growth mechanism makes the ALD with good reproducibility, excellent conformality and uniformity over the whole substrate area. In this study, TiO_2 thin films were grown by ALD on Si ,Ta ,Ti and Ni for the photoelectronchemical purposes.The effects of substrates on structure and photocurrent response were studied.

Experimental

In this work, the TiO_2 thin film were deposited by combining $TiCl_4$ and H_2O as precursors. The deposition sequence consisted of eight steps of $TiCl_4$ pulse, vacuum , Ar purge, vacuum, H_2O pulsed, vacuum , Ar purge, and vacuum.The time for each step is one second. The ALD TiO_2 film thickness was kept typically at 0.5~0.6nm as determined by ellipsometry (FiveLab－MARY-102). Field emission scanning electron microscope (FE-SEM, Philip XL-40FEG) was used to observe the film surface morphology. The crystal structure was studied by X-ray diffractometer (XRD) in the θ-2θ mode using Cu-Kα radiation (λ=1.54056Å).

Photoelectrochemical measurements were performed on an Autolab PGSTAT12 potentiostat using a three electrode setup. The reference and counter electrodes were Ag/AgCl and platinum, respectively.The TiO_2 film grown on Ta ,Ti ,Ni and Si substrates were used as the working electrode and 0.1M KOH aqueous was used as the electrolyte. In all photoelectrochemical measurements,a 100-W Mercury lamp (BLE-100S) with a 365 nm was used as the UV light source.

Results and Discussion

Fig.1 shows the X-ray diffractograms of all TiO_2 films grown at 400°C. The films contain only TiO_2 anatase phase for Si substrates but contain a mixture of anatase and rutile phases for the Ti 、Ta and Ni substrates, Fig.2 shows the morphologies of TiO_2 films. The average grain size for TiO_2 on Ti, Ta, Ni and Si are 90 ,70 ,30 and 30 nm , respectively.

Fig.3 shows the current density–voltage plots measured under UV light(wavelength=365nm) irradiation in 0.1M KOH aqueous. The scanning potential on work electrode was from positive bias to negative bias. It can be seen that there was a clear response to UV light irradiation for all samples. The larger photocurrents were observed for films grown on Ta and Ti substrates (Fig.3c and 3d). Higher rutile phase ratio and larger grain size are considered to be the cause for higher photocurrent response. The TiO_2 grown on Si substrates has the smallest photoresponse of 10.8 μA/cm^2 has due to its smallest grain size. The TiO_2 grown on Ta substrates has the highest photocurrent of 69.8 μA/cm^2 due to its larger grain size was of 70 nm and higher ratio of rutile phase.

Conclusion

A small grain size of 30nm and a low photocurrent of 10.8 μA/cm^2 were found for the TiO_2 films grown on Si substrates. In contrast, a larger grain size and higher photocurrent were found for those grown on Ni and Ta substrates. According to XRD patterns, the films grown on Ti ,Ta and Ni substrates contained rutile phase, which makes a better photocurrent response.

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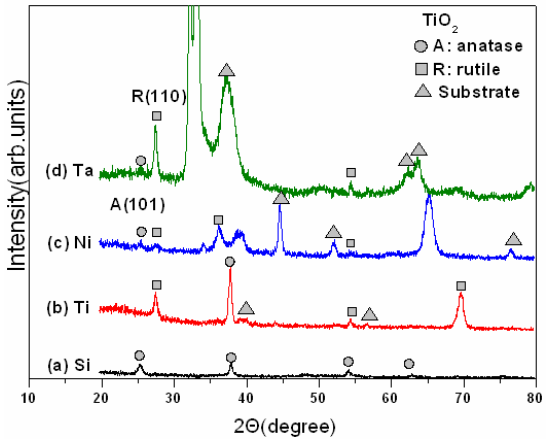

Fig.1 XRD patterns of TiO_2 films deposited on substrates of (a)Si (b)Ti (c)Ni and (d)Ta

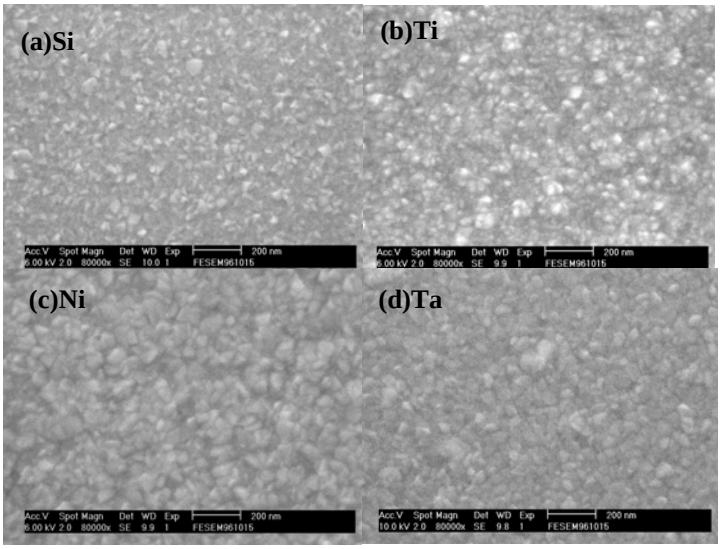

Fig.2 SEM micrographs of TiO_2 films grown on (a)Si (b)Ti (c)Ni and (d)Ta substrates

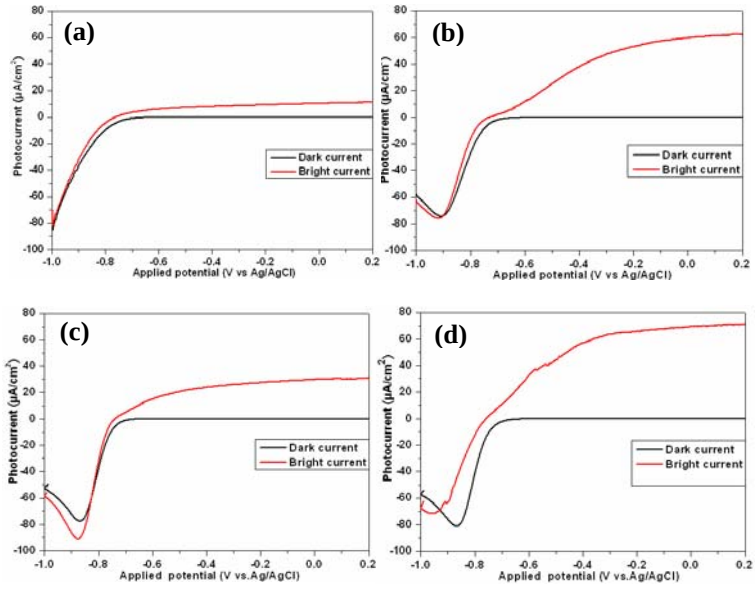

Fig.3 Linear sweep voltammograms for TiO_2 deposited on (a)Si (b)Ti (c)Ni and (d) Ta substrates. The potential scan was from positive to negative.The bright current was obtained under UV light irradiation ($3.7mW/cm^2$) and the darkcurrent was obtained without UV light irradiation.