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Efficient solar photocatalytic activity of TiO_2 coated nano-porous silicon by atomic layer deposition

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ABSTRACT

In the present study, TiO_2 coated nano-porous silicon (TiO_2/PS) was prepared by atomic layer deposition (ALD) whereas porous silicon was prepared by stain etching method for efficient solar photocatalytic activity. TiO_2/PS was characterized by FESEM, AFM, XRD, XPS and DRS UV–vis spectrophotometer. Absorbance spectrum revealed that TiO_2/PS absorbs complete solar light with wave length range of 300 nm–800 nm and most importantly, it absorbs stronger visible light than UV light. The reason for efficient solar light absorption of TiO_2/PS is that nanostructured TiO_2 layer absorbs UV light and nano-porous silicon layer absorbs visible light which is transparent to TiO_2 layer. The amount of visible light absorption of TiO_2/PS directly increases with increase of silicon etching time. The effect of silicon etching time of TiO_2/PS on solar photocatalytic activity was investigated towards methylene blue dye degradation. Layer by layer solar absorption mechanism was used to explain the enhanced photocatalytic activity of TiO_2/PS solar absorber. According to this, the photo-generated electrons of porous silicon will be effectively injected into TiO_2 via hetero junction interface which leads to efficient charge separation even though porous silicon is not participating in any redox reactions in direct.

1. Introduction

TiO_2 is widely studied semiconductor for photocatalytic applications due to its strong redox power, chemical inertness, thermal stability, and lower recombination rate of electron-hole pairs. However, the photocatalytic activity of TiO_2 is restricted to UV light due to its wide band gap energy (3.2 eV). In addition, fast recombination of photo-generated electron-hole pairs reduces the photocatalytic efficiency of the TiO_2 [1]. To overcome this, TiO_2 was modified by several metals, nonmetals and semiconductors [2–8]. Among this, semiconductor coupling is considered to be one of the best ways to alter

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the optical and electrical characteristics of TiO_2 as it can be achieved without altering the crystal structure and intrinsic characteristics of TiO_2. In a coupled semiconductor system, the low band gap of semiconductor can be excited by visible light irradiation and some of the photo-generated electrons or holes will be transferred to TiO_2 via hetero junction interface, leading to efficient charge separation [6]. The efficient solar photocatalytic activity of TiO_2 can be achieved by coupling various semiconductors such as WO_3, V_2O_5, CdSe and etc. [6–8].

Porous silicon is a low band gap semiconductor which possesses entirely different optical and electrical properties compared to bulk silicon [9,10]. Immobilization of TiO_2 on porous silicon will result in efficient solar light absorption which leads to higher photocatalytic efficiency. There are several methods available to develop TiO_2 coatings such as magnetron sputtering, chemical vapor deposition and etc [7,8]. However, these coating techniques are used to deposit coatings in line of sight on the porous substrate which leads to non-uniformed coatings inside the porous silicon. Thus, these coating techniques are not suitable to deposit uniform and conformal coatings on porous substrates.

ALD is a modified chemical vapor deposition (CVD) for growing inorganic materials in atomic level thickness control known as monolayer. In CVD, chemical vapors of precursors are pulsed simultaneously to grow thin films which are not uniform, conformal and inaccurate thickness due to gas phase reactions. In contrast, ALD is a gas phase thin film deposition technique in which chemical precursors are pulsed individually. Therefore, ALD avoids gas phase reactions between different chemical precursors during coating growth. As a result, ALD can be used to grow uniform and conformal coatings with high quality on extremely complex substrate. ALD process is also known as self-controlled process because ALD parameters such as temperature, pressure and substrate has no influence on the coating thickness other than the type of precursor used. Since constant growth per cycle (GPC) can be achieved in ALD through self-terminating gas-solid reactions of different precursors used, the thickness of the film is controlled by controlling number of deposition cycles [11–15].

Layer by layer solar absorption mechanism is proposed to explain the photocatlytic activity of TiO_2/PS (Fig. 1). According to this, Layer 1 is active to UV light and transparent to visible light. The transmitted visible light of layer 1 will be absorbed by layer 2 which is visible light active. It is well known that P-N hetero junction will be formed between P-type silicon and N-type TiO_2. Photo-generated electrons of porous silicon (layer 1) will be injected easily into TiO_2 (layer 2) via hetero junction interface, leads to efficient charge separation. Thus, photo-generated electrons of silicon indirectly contribute to TiO_2 for enhanced photocatalytic activity even though porous silicon is not participating in any redox reactions in direct. Dong Hao et al. studied the UV photocatalytic activity of TiO_2 immobilized on P type SiC foam. The result showed enhanced photocatalytic activity and confirmed that P-N hetero junction is formed between P type SiC and N- type TiO_2 which leads to higher charge separation [16]. Corbonell et al. prepared titania photonic sponges using a blend of latex spheres of different sizes and proportions as templates, and placing in the empty spaces among the latex spheres, photoactive Degussa P25 titania nanoparticles. Photonic sponge showed continuous absorption from 300 nm to 800 nm TiO_2 photonic sponge having quasi spherical voids from 2000 to 200 nm enhances by a factor of 10 the photocatalytic activity of TiO_2 [17]. Yang et al. prepared TiO_2 thin film on microstructured silicon by sol–gel technique. The microstructured silicon was produced by femtosecond cumulative laser irradiation of silicon. The result showed improved photocatalytic activity for TiO_2 coated micro structured porous silicon [18]. Sakhare et al. studied electric field assisted photocatalytic activity of TiO_2 coated porous silicon. Nano TiO_2 powder prepared by sol–gel method was successfully immobilized in porous silicon synthesized by electrochemical anodization of silicon. The result showed that negative biased photocatalytic system exhibits higher photocatalytic activity than TiO_2 under UV light irradiation [19]. Sridhar et al. studied the photoelectrocatalytic activity of ZnO grown on nano-porous silicon by atomic layer deposition. The result showed that ZnO grown on nano-porous silicon exhibited higher solar photocatalytic activity compared to ZnO grown on glass. The enhanced photocatalytic activity is attributed to visible absorption of ZnO coated nano-porous silicon [20].

The aim of this study was to prepare TiO_2 coated high surface porous silicon and check its photocatalytic and photoelectrocatalytic activity. Moreover, to the best of our knowledge there are no studies on solar photocatalytic activity of TiO_2 deposited on nano-porous silicon by atomic layer deposition. Therefore, in the present study, we made an attempt to prepare TiO_2 layer coupled porous silicon (PS) layer as an efficient solar absorber by combined technique of stain etching and ALD for enhanced solar photocatalytic activity. Layer by layer solar absorption is used to explain the enhanced solar photocatalytic activity. The surface morphology, surface roughness, crystalline phase, structure and optical property of TiO_2 coated porous

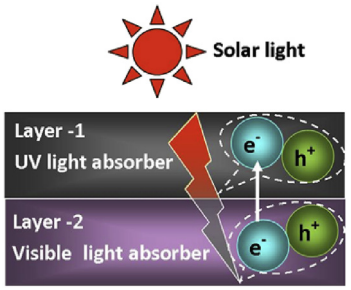

Fig. 1. Schematic diagram of layer by layer solar absorption.