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Design and fabrication of a TiO_2/nano-silicon composite visible light photocatalyst

Chun Yu Lin[a], Yean Kuen Fang[a,*], Che Hao Kuo[a], Shih Fang Chen[a], Chun-Sheng Lin[a], Tse Heng Chou[a], Yu-Hua Lee[b], Jui-Che Lin[c], Sheng-Beng Hwang[d]

[a] *VLSI Technology Laboratory, Institute of Microelectronics, Department of Electrical Engineering, National Cheng Kung University, Taiwan*
[b] *Department of Physics, National Cheng Kung University, Taiwan, Taiwan*
[c] *Department of Chemical Engineering, National Cheng Kung University, Taiwan*
[d] *Department of Electrical Engineering, Chien Cuo Technology University, Taiwan*

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Abstract

Nano-silicon (nc-Si) was utilized as the charges generator to promote the photocatalytic and super-hydrophilic reactivity of TiO_2 film under visible light irradiation. The photocatalytic ability of TiO_2/nc-Si composite photocatalyst was evaluated by a set of experiments to photodecompose 100 ppm methylene blue (MB) in aqueous solution. And the super-hydrophilic property was characterized by measuring the water droplet contacts angle, under visible light irradiation in atmospheric air and at room temperature. Under 100 mW/cm^2 visible light irradiation, the droplet contact angles were reduced to 0° within 4 h with nc-Si charge generator. Additionally, the rate constant of MB photo-degradation was promoted 6.6 times.

Keywords: Nano-silicon; TiO_2; Photocatalyst; Methylene blue; Super-hydrophilic

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1. Introduction

TiO_2 as a photocatalytic or hydrophilic material has been investigated extensively [1–3]. The good photocatalytic or hydrophilic property of TiO_2 owes to its high chemical stability and low recombination rate of photoexcitated electron-hole pairs [3]. However, only the UV light can activate the photocatalytic function in conventional TiO_2 catalyst thus practically ruling out the utilization of sunlight or indoor lighting as an energy source for the photoreaction. On the other hand, the intensity of UV light from the fluorescent tube is only 0.1–1 μW/cm^2, which is not enough for most applications. Hence, visible light photocatalyst is necessary for indoor uses. In the past, many studies related to improve the photocatalytic reactivity of TiO_2 under visible light irradiation have been reported [4–7] For example, using WO_x/TiO_2 binary oxide composites [4], doping transition metal into TiO_2 [5,6] or doping nitrogen into the substitution sites of TiO_2 [7]. In these studies, the utilization of a rough surface morphology of TiO_2 to improve the photocatalytic and hydrophilic properties has been ignored. However, which is a crucial factor in the photocatalytic applications [8]. It was found the TiO_2 with porous structure using photoelectrical etching or with very fine particles possesses superior photocatalytic activity [9,10]. Which is supposed due to the enlarged reacting area in these structures. Nevertheless, the porous structure also suffers the inferior mechanical properties such as adhesion and hardness simultaneously [11].

In this work, we roughened the surface morphology of TiO_2 by incorporating the nanocrystalline silicon (nc-Si) into TiO_2 photocatalyst to construct a TiO_2/nc-Si/a-Si composite layer on glass substrate as visible light photocatalyst. Experimental results show the improvement of the photocatalytic and super-hydrophilic reactivity of TiO_2/nc-Si/a-Si composite photocatalyst under visible light irradiation very significantly. The improvement mechanism and details of design considerations are described in the next section.

2. Design considerations and operation mechanism

In this study, the visible light photocatalyst samples were prepared with structure of TiO_2/nc-Si/a-Si/glass as illustrated

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* Corresponding author. Tel.: +886 6 2080398; fax: +886 6 2345482.
E-mail address: ykfang@eembox.ee.ncku.edu.tw (Y.K. Fang).

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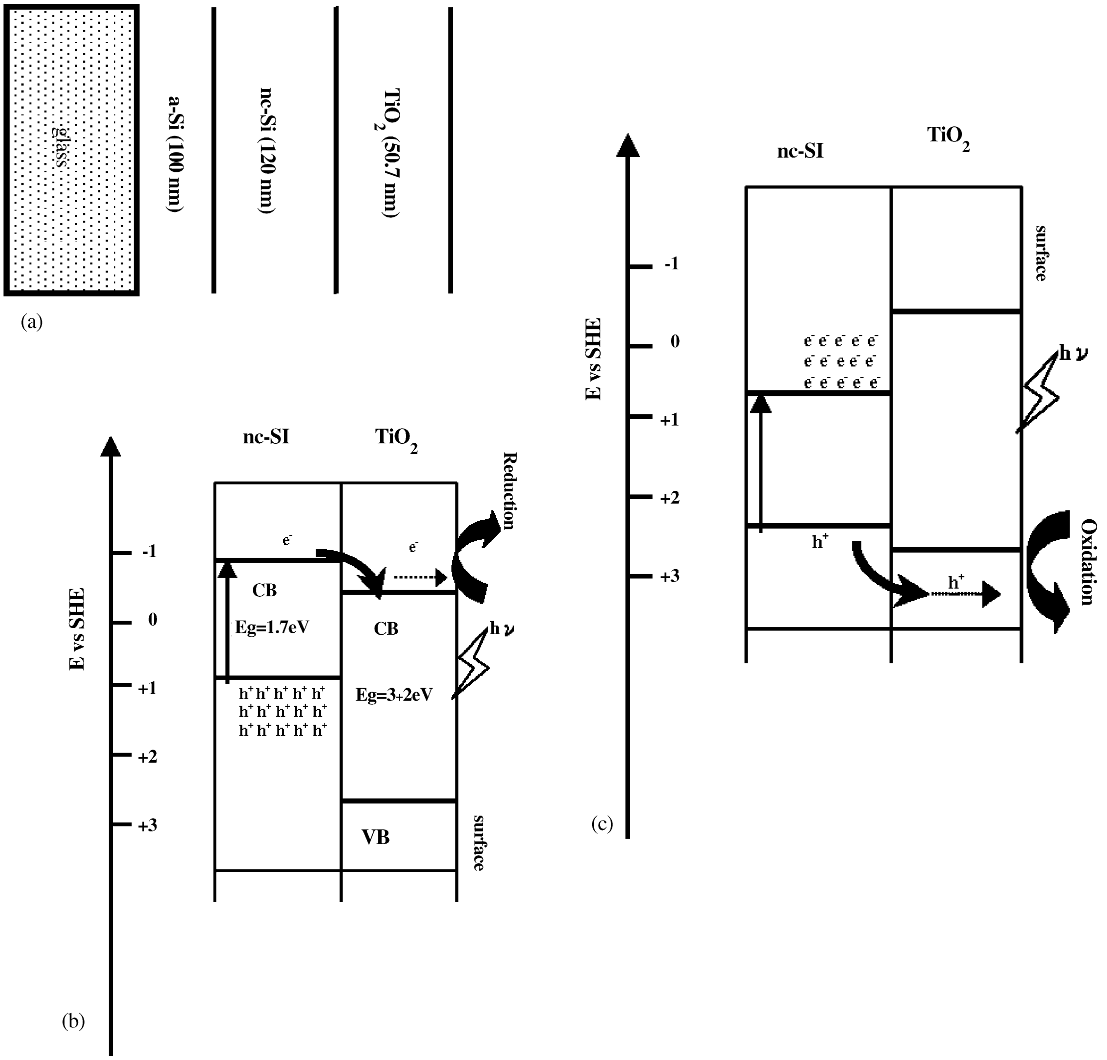

Fig. 1. (a) Schemetical diagram of TiO_2/nc-Si/a-Si/glass photocatalyst. (b) Energy band diagram of photocatalyst and the transfer of light generated electrons. (c) Energy band diagram of photocatalyst and the transfer of light generated holes.

schematically in Fig. 1(a). The structure was designed in base of the following considerations. (A) Use glass as substrate. Glass is a popular substrate for TiO_2 photocatalytic applications, such as anti-fogging, self-sterilizing and self-cleaning etc, it was adopted in this study. (B) Use nc-Si as visible lights absorber. TiO_2 is a wide energy bandgap ($E_g = 3.2$ eV) semiconductor, only absorbs lights below a threshold wavelength ($\lambda = 387.5$ nm), hence a material with $E_g < 3.2$ eV should be incorporated to adsorb visible lights for generation of electron–hole pair. The nc-Si with band-gap of 1.1–1.7 eV was adopted for visible lights absorber for the advantages of high mobility, better optical absorption transfer efficiency [12–14], and finer particles and can be deposited on glass substrate under low temperature. Especially, the structure with finer particles can be used to assist the top thin TiO_2 (≤ 100 nm) film forming with grain-like structure for increasing surface area. (C) Use a-Si as buffer layer to improve the adhesion on glass substrate. It is well known, a-Si can be deposited with low temperature on glass substrate with strong adhesion for optical devices [15,16], therefore to remedy the poor adhesion issue of porous structure; we employed the a-Si buffer layer for improving the adhesion of TiO_2/nc-Si composite layer to glass substrate. Moreover, we have found the a-Si can enhance the aggregation of finer crystal particles during the deposition of nc-Si film thus in turn the higher grain-like structure of TiO_2 to get larger reaction area [17]. (See the SEM photos in the inset of Fig. 5a and b).

Next, it has been reported the origin of photocatalytic and super-hydrophilic reactivity of TiO_2 is the generation of OH^- [18] and/or $>Ti^{IV}OH^{\bullet}+$ [19] on TiO_2 surface. Both OH^- and $>Ti^{IV}OH^{\bullet}+$ radicals are rather reactive and as key species to degrade many classes of organic materials such as methylene blue (MB) [20], and decompose hydrophobic molecule [21]. As shown in Fig. 1(b), the band diagram of TiO_2/nc-Si composite layer, both conduction band (CB) and valance band (VB) of TiO_2 are lower than that of nc-Si. Under irradiation of lights (UV + visible), the electron–hole pairs are generated in the nc-Si VB initially, and the electrons transfer to the CB of TiO_2, while holes accumulated in the interface of nc-Si/TiO_2 for the lower energy VB of TiO_2. Then oxygen on the TiO_2 surface