EFFECTS OF BUFFER LAYER ON THE SURFACE MORPHOLOGY OF ZINC TIN OXIDE (ZTO) NANOSTRUCTURE

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Abstract

The surface morphology of photoanode materials is a crucial role for the utilizing as an active layer in dye sensitized solar cell (DSSC). The formation of surface morphology of zinc-tin oxide (ZTO) nanocomposite depending on the various buffer layer were investigated in this study. ZTO on three different buffer layer such as zinc oxide (ZnO), titanium dioxide (TiO_2) and ZTO was grown by chemical bath deposition (CBD) method. The effects of growth time on the structural properties of nanocomposite were also examined by varying the growth time including 5, 10 and 15 h in the CBD process. The structural and morphological properties of the nanocomposite were confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM) results. It was found out that the different surface morphology of ZTO was obtained depending on materials of buffer layers. The increasing the growth time, the intensity of ZnO and TiO_2 peaks were also increased in ZTO film. The formation of ZTO composite seemed to be larger 15 h than 5 h and 10 h. The influence of different seed buffer layer on the growth of ZnO-TiO_2 composite structure was observed by the variation of morphologies. Nonoparticles, nanoflake and mixed nanostructure were formed for the films ZTO/ZnO, ZTO/TiO_2 and ZTO/ZTO grown by CBD method.

Keywords: chemical bath deposition (CBD), growth time, nanoflake, nanoparticles, surface morphology, ZTO film

Introduction

The buffer layer significantly influences the surface morphology of nanostructures grown by the chemical bath deposition (CBD) method. The buffer layer can act as a nucleation site for promoting uniform nucleation and growth of nanostructures. An aluminum (Al) buffer layer facilitated the formation of uniformly distributed zinc oxide (ZnO) nanoflakes by reducing the nucleation barrier (Lahewil *et al.*, 2021). The type and thickness of the buffer layer can control the orientation and structure of the nanoparticles. ZnO nanowires grown on different thicknesses of ZnO seed layers show variations in their alignment and density (Azmi, Z.H *et al.*, 2022). The buffer layer can improve the homogeneity of the nanoparticle surface. Proper surface preparation and choice of buffer layer material are crucial for achieving a uniform morphology (Bolshakov A D *et al.*, 2019). The buffer layer can also affect the crystallinity of the nanoparticles. Studies have shown that different buffer layer materials and thicknesses can lead to variations in crystal quality and surface morphology (Bolshakov A. D *et al.*, 2019). These effects are essential for tailoring the properties of nanoparticles for specific applications in electronics, optoelectronics, and energy devices.

One dimensional nanostructure such as rods, wires, and flakes are among the most promising nanostructures for the wide range of applications in electronic, optoelectronic, nanophotonic, electrochemical, and electromechanical devices due to their unique features. ZnO and TiO_2 are the most applicable materials due to their outstanding properties such as wide direct bandgap, large exciton binding energy at room temperature, and high electron mobility. Both

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metal oxides possess common properties such as wide energy band gaps, nontoxic compounds, chemical stability, and inexpensive.

Recently, chemical bath deposition (CBD) method is largely used for the synthesis of nanostructures since it can provide different morphologies and different properties of the product. The types of precursor, solvent, substrate and solution process parameters such as growth time, and temperature, are important parameters in this method. Among them, type of buffer layer in CBD method is one of the most important parameters since growth of thin film on the bare substrate is inevitable. Without buffer layer, lattice mismatch between the glass or glass-coated substrate and epilayer can be increased. In this paper, ZnO, TiO_2, and ZnO-TiO_2 buffer layers on glass substrate are deposited by spin coating method. The structural and morphological properties of ZnO-TiO_2 composite nanostructure grown on different buffer layers investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM) are discussed.

Experimental Details

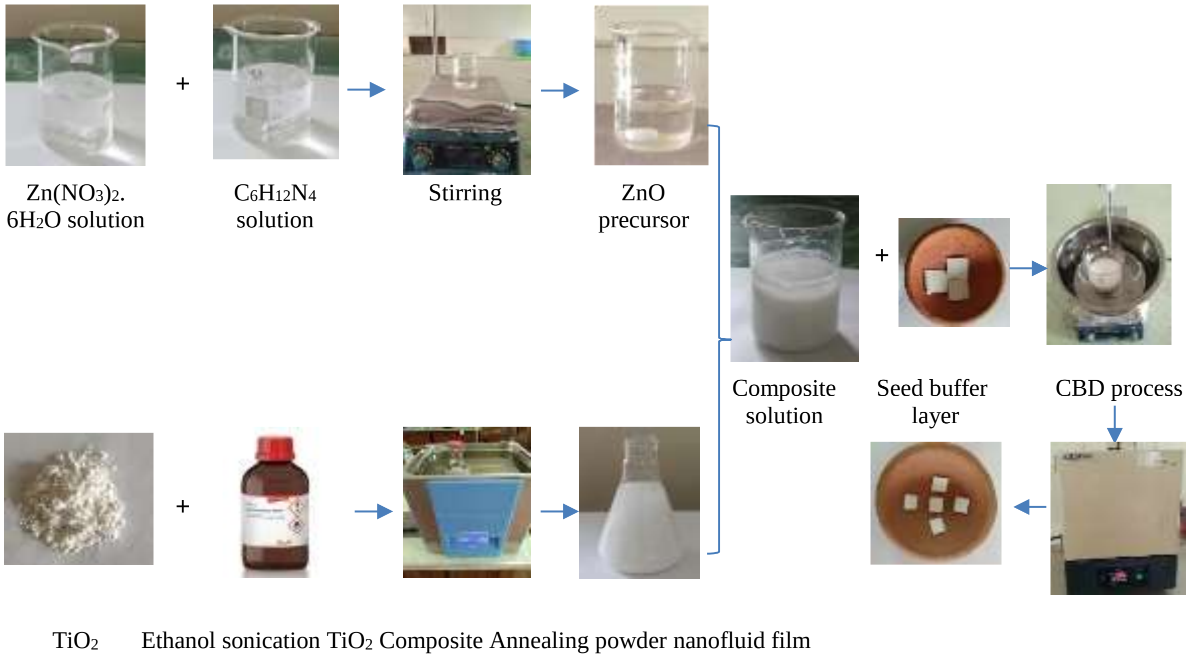


Figure 1. Synthesis photograph of ZTO composite films by CBD method

Preparation of Buffer Layer

To prepare different seed (buffer) layers, firstly glass substrates (1-inch square) were cleaned in a solution of ethanol, acetone, isopropanol, and distilled water (DW) by sonication. For ZnO and TiO_2 buffer layer, 1 g of ZnO or TiO_2 particles and 4 μL of ethanol were mixed and stirred for several days in order to form the well dissolved paste. For the preparation ZTO paste, the powders of 1 g ZnO and 1 g TiO_2 are dissolved in 8 μL of ethanol and stirred for several days. 200 μL of each paste was coated onto the glass substrates by two step-spin coating method at 3000 rpm for 30 min each. The coated ZnO, TiO_2 and ZnO-TiO_2 films were annealed at 500 ºC for 1 h. Finally, different buffer layers were successfully obtained.

Preparation of Composite Films on Buffer Layers

For the ZnO precursor solution, zinc nitrate hexahydrate, $Zn(NO_3)_2{\cdot}6H_2O$ (0.05 M) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) (0.05 M) precursors were separately prepared at the same concentration. These two precursors were mixed at a ratio of 1:1 volume ratio and stirred for 1 h in order to form homogeneous ZnO precursor. For the preparation of TiO_2 nanofluid, 1 g of TiO_2 powder was dissolved in 70 mL of ethanol and sonicated for 4 h in order to mix the homogeneous solution. For the composite solution, 1:1 volume ratio ZnO precursor and TiO_2 nanofluid were mixed together and they were stirrer for 1 h.

Preparation of ZTO Films by Chemical Bath Deposition (CBD) Method

For CBD growth, each buffer layers prepared by previous step was put vertically inside the composite solution and placed into the oil bath at a fixed temperature 90 ºC and grown for 5, 10 and 15 h, respectively. After the growing, the composite films were rinsed in DI water in order to remove any contamination. After that, the films were dried at room temperature. Finally, the ZTO composite films were annealed at 500 ºC for 1 h. Finally, three types of films such as ZTO/ZnO, TiO_2/ZnO and ZTO/ZTO were successfully received. Synthesis photograph for the preparation ZnO-TiO_2 composite films is displayed in Figure 1.

Results and Discussion

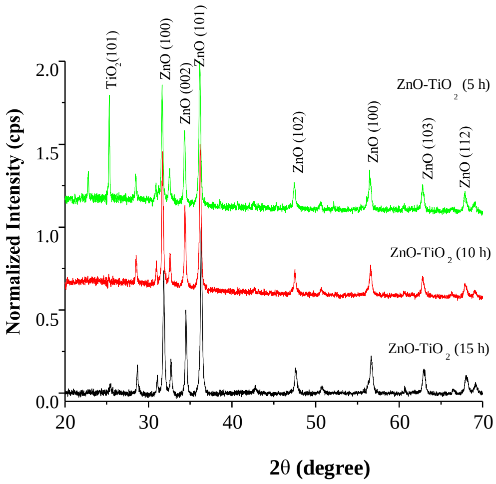


Figure 1 XRD spectrum of ZTO/ZnO film at different CBD growth time

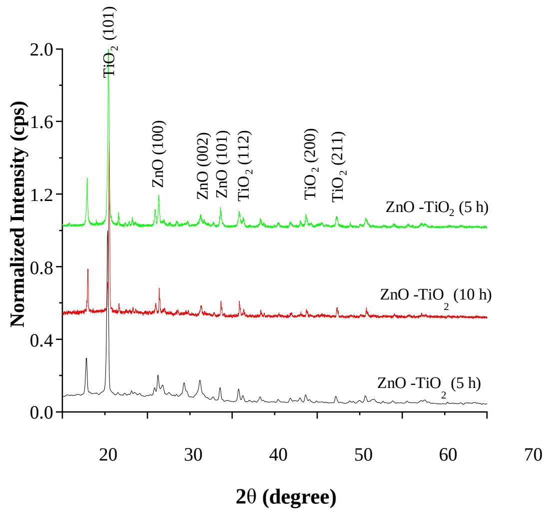


Figure 2 XRD spectrum of ZTO/TiO_2 film at different CBD growth time

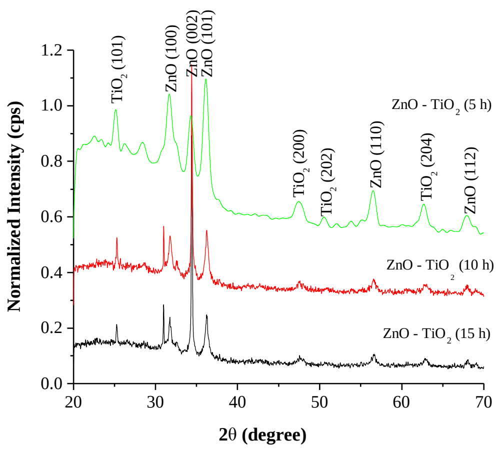


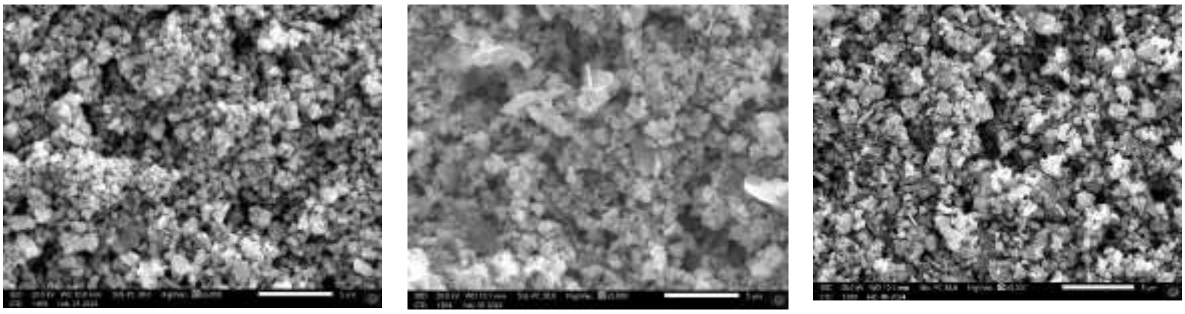
Figure 3 XRD spectrum of ZTO/ZTO film at different CBD growth time

XRD measurement was performed in order to identify the target materials. The diffraction angle 2θ degree at 31.6˚, 34.3˚, 36.2˚, 47.4˚, 56.4˚, 62.7˚, 66.1˚, 67.7˚& 68.8˚ are attributed to (100), (002), (101), (102), (110), (103), (200), (112) & (201) planes of the hexagonal crystalline structure (DB card number 9004180). The diffraction angle 2θ degree at 25.2˚, 36.9˚, 37.9˚, 38.6˚, 47.6˚, 53.9˚, 55.1˚62.1˚, 62.7˚& 68.7˚of the reflection (101), (103), (004), (112), (200), (105), (211), (213), (204) & (116) planes (DB card number 9008216) are anatase TiO_2. The amalgamation of anatase TiO_2 and hexagonal wurtzite ZnO in the mixed oxide system were also observed in all XRD spectra.

XRD spectra of ZTO films grown on ZnO, TiO_2 and ZnO-TiO_2 buffer layers at different growth times are shown in Figure 2, 3 and 4. In Figure 2, three most intensity peaks from (100), (002) and (101) were the characteristic peaks of ZnO. In addition, only TiO_2 peak from (100) is observed for 5 h growth time. When the growth time was increased to 10 h and 15 h, the peak from all ZnO peaks were also drastically increased and TiO_2 peaks was relatively decreased. Two ZTO peaks were observed.

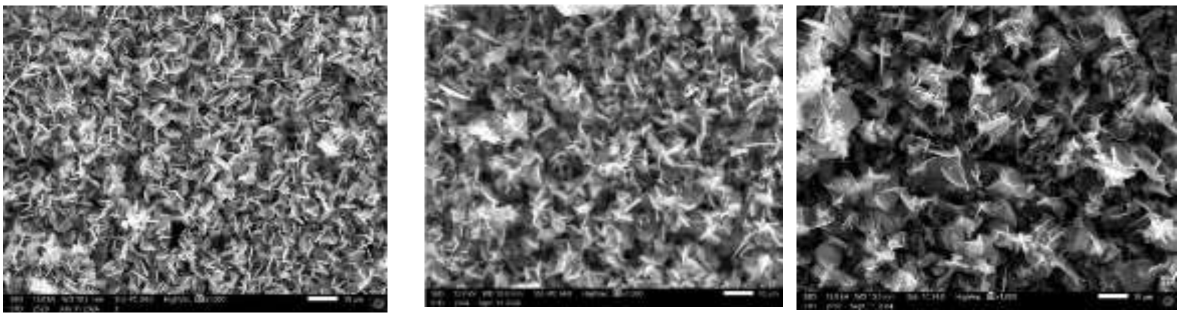
In Figure 4, all ZnO peaks from (100), (002) and (101) were drastically decreased. In addition, only TiO_2 peak from (100) is observed for 5 h growth time. When the growth time was increased to 10 h and 15 h, the peak from all ZnO peaks were also drastically increased and TiO_2 peaks was relatively increased. Again, for the ZTO composite film on ZTO buffer layer, the intensity of ZnO peaks were higher than that of TiO_2. However, the intensity of all single peak of ZnO and TiO_2 peaks were smaller than those in ZTO/ZnO and ZTO/TiO_2 films. Six ZTO peaks were occurred for the growth time 10 and 15 h.

The SEM analysis is carried out in order to observe the surface morphology of each film depending on the various growth time. The SEM images of ZTO/ZnO films are exhibited in Figure 5. Only particles were observed. The particle size was bigger when the growth hour was increased. In Figure 6, only the flake structure was formed for the ZTO/TiO_2 films. Similarly, the flakes were bigger while increasing the growth time. When the composite films were deposited on ZTO buffer film, mixed morphology comprising of both ZnO particles and TiO_2 flake was observed. The more increasing the growth time, the more particles were formed since the ZnO peak became more prominent and TiO_2 flake were the less.



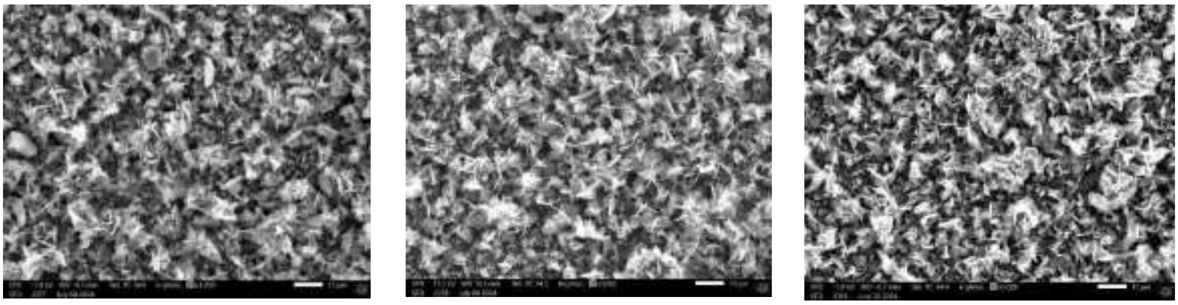
(a) (b) (c)

Figure 5 SEM images of ZTO film onto the ZnO buffer layer at the CBD growth time (a) 5 (b) 10 and 15 h



(a) (b) (c)

Figure 7 SEM images of ZTO film onto the TiO_2 buffer layer at the CBD growth time (a) 5 (b) 10 and 15 h



(a) (b) (c)

Figure 6 SEM images of ZTO film onto the ZTO buffer layer at the CBD growth time (a) 5 (b) 10 and 15 h

Among the structures, nanoflakes have two-dimensional (2D) and nanoparticles have one-dimensional (1D) nanostructures. Both structures have larger surface area which facilitates more efficient electron pathways and reduces recombination losses. Although both nanostructures can enhance efficiency of dye sensitized solar cell (DSSC), nanoflakes may offer better electron transport and light absorption properties. This may potentially lead to higher efficiencies of DSSC. However, the choice between nanoparticles and nanoflakes should be based on the specific requirements and design of the DSSC.

Conclusions

The surface morphologies of ZnO-TiO_2 (ZTO) composite films depending on different buffer layers grown by chemical bath deposition (CBD) method were discussed. The films grown on ZnO buffer resulted the particles. On the other hand, the flakes structure was attained when the films grown on TiO_2 buffer layer. Mixed morphology of both particles and flakes were acquired for the ZTO buffer layer. These different morphologies of the films were reflected from particular buffer layer used in CBD growth. Therefore, it can be concluded that types of materials for buffer layer are essential parameters for the formation of epilayers like particles, flakes and mixing of both particles and flakes in CBD method. Since nanoflakes can scatter light more effectively within the solar cell, higher photocurrent and better overall efficiency can be available for the ZnO-TiO_2/TiO_2 film. Therefore, this work can be applied as a photoanode materials in DCCS.

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