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Application of ZnO Single Crystal Rods as Anti-Reflective Material for PV Cells

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In this study, ZnO nanorods for antireflection coatings application to the silicon solar cells were epitaxially grown over the Si substrate using both thermal evaporation method and wet chemical method and their characteristics were investigated. A precursor for the thermal evaporation method was prepared by impregnating zinc acetate over the activated carbon at three different loading amounts: 10, 20, and 30 wt%. The temperature for the epitaxial growth of ZnO nanorods over the substrate was fixed to 850°C. The diameter of the synthesized single crystalline ZnO nanorods was about 1 μm. The shape and size of the ZnO nanorods varied with the content of the precursors loaded over the activated carbon. The length of the ZnO nanorods increased as the loading amount of the zinc was increased. Single crystalline ZnO nanorods were grown over the substrates by a hydrothermal synthesis in an autoclave reactor. Zinc nitrate was used for the precursor material in the wet chemical method. The length and diameter of the ZnO nanorods synthesized by the wet chemical method were about 200 nm and a few nm, respectively. The surface morphology of the ZnO nanorods prepared by two growth methods was observed by scanning electron microscope. Its crystal structure was analyzed by an X-ray diffraction spectrometer. The optical properties, such as reflectance, were measured by the UV-Visible spectrophotometer. It was confirmed that ZnO nanorods decrease the reflectance of UV and Visible lights. Therefore, it was concluded that ZnO nanorods can be used as the antireflective material for photo voltaic cells.

Keywords antireflection coatings; zinc oxide nanorods; solar cells; thermal evaporation method; wet chemical method

Introduction

Constantly increasing demand of renewable and nonpolluting energy production methods has made solar cells one of today's hottest research areas. Developing more cost-effective fabrication methods that enable production of extremely non-reflecting surface is one of the key issues in solar cell research [1–3]. Many other applications, such as miniaturized chemical analysis systems, would also benefit greatly from low-cost surface with low and uniform reflectivity [3,4]. Typically, suppression of Fresnel reflection has been achieved by

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antireflective coatings, but they suppress reflection efficiently only in a narrow wavelength range. Suppression of reflection over a broad spectral range can be achieved by using nanotextured surfaces that form a graded transition of the reflective index from air to the substrate [1,2,5–12].

Antireflection coatings (ARC) have been widely used to substantially increase the efficiency of the solar cell by reducing the surface reflection of the sun light. It is known that ARC is significantly effective in reducing the reflection at the solar cell surface. In general, TiO_2, SnO_2, and ZnO are used for ARC materials in either single or multilayer structure. Single crystalline ZnO is transparent at room temperature and has electrical conducting properties. Another approach has been adopted to improve their optical properties. Surface texturing has been widely applied to crystalline silicon solar cells, using anisotropic etching [3]. Lee et al. [13] reported that polymer nanorods were applied to AR coating for the solar cells and that they achieved an improvement in efficiency. In this study, single crystalline ZnO nanorods were epitaxially grown on the silicon substrates in order to determine the possible application to the silicon solar cells for the improvement of efficiency instead of the texturing. The crystal structure, morphology, and reflectance of ZnO nanorods grown by thermal evaporation and wet chemical methods were characterized with the aid of X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-visible spectrophotometer.

Experimental

In this study, ZnO nanorods for ARC application to the silicon solar cells were grown over the substrate using both thermal evaporation method and wet chemical method. When tested with the thermal evaporation method, the solid precursor was prepared by the following procedure: dissolving zinc acetate into the distilled water and mixing it with activated carbon, then dehydrating, and drying. Silincon wafers containing thermally oxidized SiO_2 layers (1000 Å thickness) were used as the substrates. The substrates were chemically cleaned according to a standard acetone, methanol, and deionized water (AMD) procedure. The substrates were completely dried by using nitrogen gas prior to the deposition of the ZnO nanorods.

Thermal Evaporation Method for the Growth of ZnO Nanorods

As shown in Fig. 1, a precursor was prepared by impregnating zinc acetate (Aldrich, 98%) over the activated carbon (Aldrich). First, a precursor solution was prepared by dissolving zinc acetate into the distilled water by varying the loading amount of zinc acetate from 10, 20, to 30 wt%. The pretreated activated carbon and the prepared zinc acetate solution were mixed by a rotary vacuum evaporator at 45°C for 4 h. The particle sizes of activated carbon was in the range of 150–200 μm in diameter and those particles were completely dried for 12 h at 150°C prior to the impregnation of zinc acetate. Then, the mixture was dehydrated for 12 hours to remove the moisture from the material at 110°C.

ZnO nanorods were epitaxially grown over the substrates using a thermal evaporation method. Figure 2 shows a schematic diagram of our experimental setup. Nitrogen was used for a carrier gas and it contained 2 vol% of oxygen. Oxygen contained in the carrier gas was used for the partial oxidation of the activated carbon and the oxidation of zinc evaporated at high temperature condition. Temperature was increased from room temperature to 850°C at a rate of 40°C/min. The reactor was maintained at 850°C for 2 hours. When the epitaxial

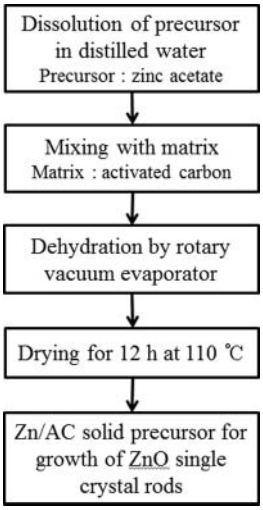

Figure 1. Preparation of Zn/AC solid precursor for growth of ZnO single crystal rods by thermal evaporation method.

growth of single-crystalline ZnO was complete, the reactor was cooled down and the sample was collected to investigate the characteristics of the prepared samples.

Wet Chemical Method for the Growth of ZnO Nanorods

Single crystalline ZnO nanorods were grown over the substrates by a hydrothermal synthesis in an autoclave reactor. Figure 3 shows a schematic diagram of our experimental setup. In this study, zinc nitrate was used as the precursor material for the wet chemical method. For ZnO nanorod growth, a precursor solution was prepared by dissolving 0.0025 M zinc nitrate into the distilled water. In order to increase the pH level of solution by approximately

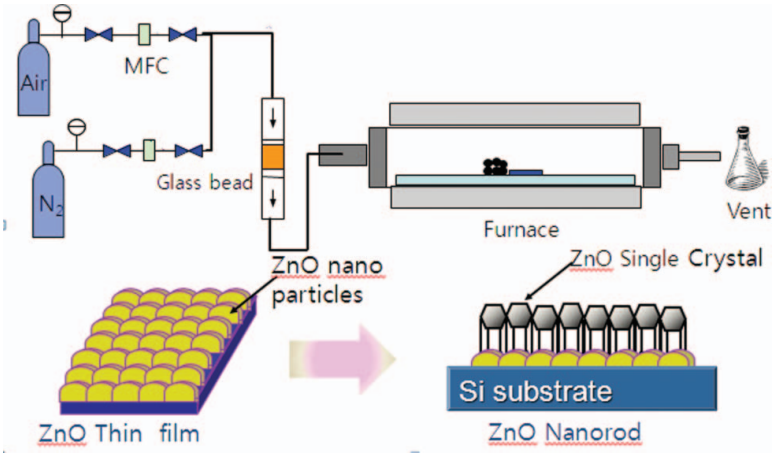

Figure 2. Schematic diagram of experimental apparatus for growth of ZnO single crystal rods by thermal evaporation method.

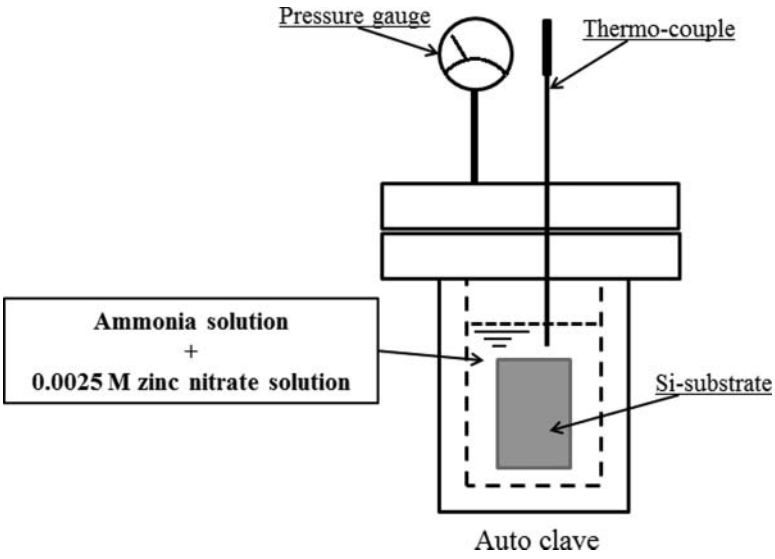

Figure 3. Schematic diagram of experimental apparatus for growth of ZnO single crystal rods by wet chemical growth.

10, ammonium hydroxide was added to the Zn-precursor solution. The prepared silicon substrate, in which the ZnO thin film was deposited by sputtering, was placed in the reactor. After aging the sample for 24 h, it was heated at 95°C for 1 and 2 h. Antireflection properties of ZnO nanorods were investigated in terms of growth period in this study.

Characterizations of ZnO Nanorods

The surface morphology of the ZnO nanorods prepared by two growth methods was observed by scanning electron microscope (SEM, HITACHI S-4800). Its crystal structure was analyzed by an X-ray diffraction spectrometer (XRD, Panalytical, MPD for thin film). The optical properties, such as reflectance, were measured by the UV-Visible spectrophotometer (Ocean Optics Inc, USB 4000 optic spectrometer) under the field of UV and visible rays.

Results and Discussion

SEM Analysis

In our previous study [14–16], the epitaxial growth of ZnO nanowires for optical devices was carried out by the thermal evaporation method. The length and diameter of the ZnO nanowires varied with the content of the zinc precursors loaded over the activated carbon. The length of the ZnO nanowires increased as the amount of the precursor loaded over the activated carbon was increased, while their diameter decreased. On the other hand, when the contents of zinc contained in the precursor were low, the length of the single crystalline ZnO nanorods was short and the diameter was exceedingly thick. When the contents are low, the diameter is about 1 μm and when the contents are high, it is about 150nm; it has been reported that these lengths can grow about 1–2 μm. Several different types of ZnO were formulated at various temperatures. That are, ZnO like nano-rod at 700°C, ZnO

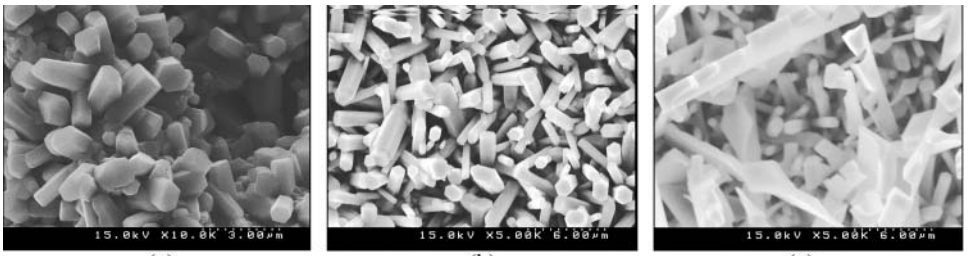

Figure 4. SEM images of ZnO single crystal rods grown by thermal evaporation of Zn/activated carbon used as precursor; (a) 10 wt% Zn/AC, (b) 20 wt% Zn/AC, and (c) 30 wt% Zn/AC.

nano-wire at 800°C, ZnO like needle was formed above 900°C. From these results, it was known that the type of ZnO is different in accordance with the synthetic temperatures. Shape of nano-structure was changed from rod to wire and then needle as temperature increased. If the ZnO thin films were deposited as a buffer layer on the substrate, ZnO nanorods were epitaxially grown over the buffer layer without using any metallic catalysts. However, ZnO nanorods were not epitaxially grown unless the buffer layer was deposited over the substrate. Instead, either nanorods or nanowires existed in the center of the tetrapod structure, starting a nucleation. Based on experimental results, it is believed that the most critical effect to the growth of ZnO nanorods are the properties of the buffer layer deposited on the substrate, instead of, the type of substrate. The tetrapod structure is considered as a typical polycrystalline structure. It was indicated that the polycrystalline ZnO would form in the center of the tetrapod structure starting a nucleation. From our previous work[14], the optimum temperature for the epitaxial growth of ZnO was around 850°C. In this study, the growth of the ZnO nanorods was performed with the new precursor prepared by the impregnation method. The precursor was prepared by impregnating zinc acetate over the activated carbon at three different loading amounts: 10, 20, and 30 wt%. Approximately 10–30 wt.% of zinc acetate was loaded over the activated carbon. The temperature for the epitaxial growth of ZnO nanorods over the substrate was fixed to 850°C. Figure 4 shows the SEM images of the ZnO nanorods synthesized by the thermal evaporation method with three different loading amounts of zinc acetate. From the figure, it is observed that the shape and size of the ZnO nanorods varied with the content of the precursors loaded over the activated carbon. In previous study [15], the length of the ZnO nanorods increased as the loading amount of the zinc was increased. However, the ZnO nanostructure was grown as a flower like structure, which is consisted of ZnO single crystal rods of about 3 μm length, in this study and its length increased with increasing loading amount of zinc over activated carbon, as shown in Fig. 4(a) and (b). Meanwhile, the morphology of ZnO nanostructure grown 30 wt.% of zinc over activated carbon was observed to differ with other ZnO structure as shown in Fig. 4(c) and the color of ZnO nanorods was white. It was believed that the white color of ZnO nanostructure appear because the coupled parts connected between the single-crystalline nanorod and the buffer layer form polycrystalline structure. In our previous study [15,16], it had been confirmed by XRD analysis that these crystalline is the single crystal ZnO.

The morphologies of ZnO nanorods synthesized by the wet chemical method are presented in Fig. 5. As shown in Fig. 5, their length and diameter were about 100 nm and a few nm, respectively. Furthermore, it was identified that when the growth period was maintained for two more hours, the length and the diameter of the single-crystalline zinc oxide was longer. When examined with the naked eye, the single-crystalline zinc oxide

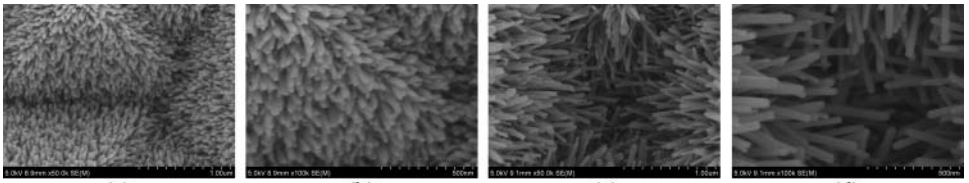

Figure 5. ZnO single crystal nanorods grown by wet chemical method, (a) growth time: 1 h, magnification X 50,000, (b) growth time: 1 h, X 100,000; (c) growth time: 2 h, X 50,000, (d) growth time: 2 h, X 100,000.

synthesized by the wet chemical method appeared to be transparent. This is because most exist as single crystalline form instead of polycrystalline structure.

XRD Measurement

The crystalline structure of the ZnO nanorods synthesized by the thermal evaporation method was determined by an X-ray diffractometer. Figure 6 shows the XRD patterns of the ZnO nanorods grown on the silicon substrates at all three different loading amounts of zinc acetate. In Fig. 6, XRD patterns confirmed the formation of polycrystalline ZnO. Polycrystalline ZnO shows particular XRD peak patterns depending upon the crystalline orientation. The angle and intensity of XRD peaks for polycrystalline ZnO are at 31.7° (100), 34.5° (002), and 36.2° (101). There was a tendency to increase XRD peak intensity as the loading amount of zinc precursor over the activated carbon increased. When 10 wt% of zinc acetate was loaded over the activated carbon, XRD peak intensity ratio on the (002) plane was relatively higher than those on the (002) plane in the other two loading amounts. Meanwhile, XRD peak intensity ratio on the (002) and (101) planes was increased when the

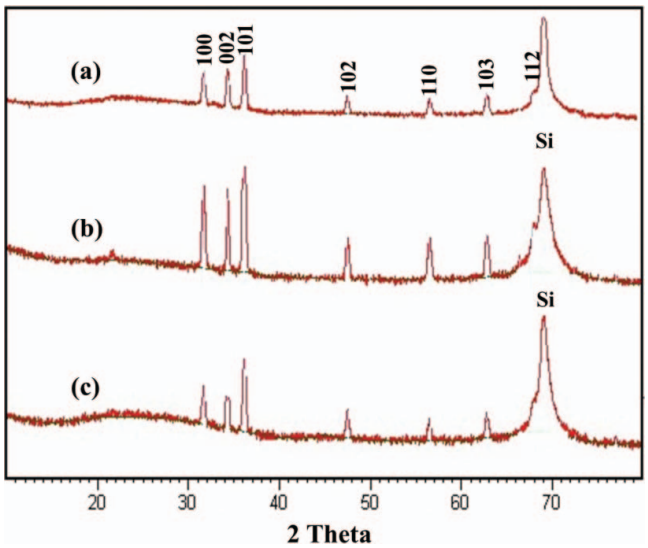

Figure 6. XRD patterns of ZnO nanorods grown by thermal evaporation of Zn/activated carbon used as precursor; (a) 10 wt% Zn/AC, (b) 20 wt% Zn/AC, and (c) 30 wt% Zn/AC.

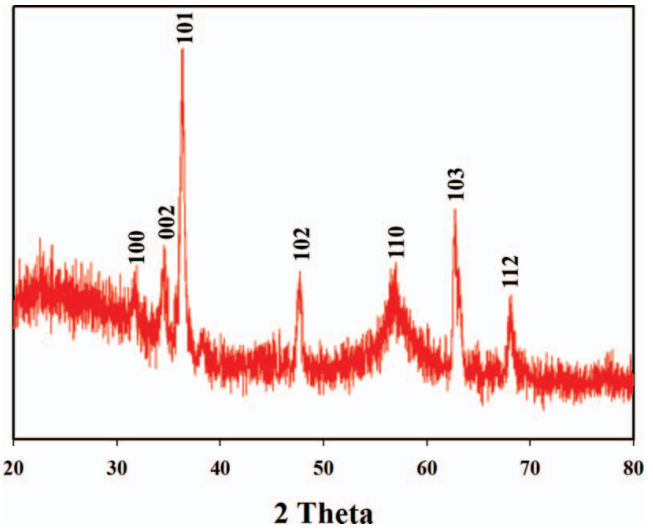

Figure 7. XRD patterns of ZnO nanorods grown by wet chemical method.

higher content of zinc acetate was loaded over the activated carbon. It is indicated that the polycrystalline ZnO was formed at higher zinc content. Consequentially, the polycrystalline structures were formed by the fusion of zinc rods at a boundary of contact. We believed that the loading amount of zinc should be optimized to obtain the uniform growth of the single crystalline ZnO nano rods.

The phase and crystalline orientation of the ZnO nanorods synthesized by the wet chemical method were also determined by XRD. In the XRD patterns, the high intensity peak corresponding to the (101) orientation at $2\theta \approx 36.2^{\circ}$ was observed in the ZnO nanorods synthesized by the wet process, as shown in Fig. 7. This result confirmed that the ZnO nanorods grown on the silicon substrates consisted of typical single-crystalline ZnO. Single-crystalline ZnO is a substance that has high transparency. Considering the fact that the transparency can be examined with the naked eye, it developed into the single crystal. Because Si based solar cells conduct electricity from the radiation in the range of UV to visible light region, transparency of substrate is very important. As an antireflection coating, it is more favorable for single-crystalline ZnO to have transparent property. In the thermal evaporation method, the loading amount of zinc should be properly controlled to achieve the epitaxial growth of single crystalline ZnO nanorods.

Reflectance of ZnO Single Crystal Rods

In order to investigate the effect of ZnO nanorods on the antireflection performance, the reflectance of the ZnO nanorods prepared in this study was measured in the wavelength range of 220 nm to 700 nm as shown in Fig. 8 and 9. The reflectance of Si substrate shows a maximum value of 40% at 280 nm, while the reflectance in the visible spectrum shows a relative low reflectance. The reflectance of the Si substrates coated with ZnO thin film was reduced both in UV region and visible light region. The reflectance of less than 20% is observed in UV region. Meanwhile, while the reflectance of single-crystalline zinc oxide nanorods developed on substrate decreased within 10% in the ultraviolet ray region, it increased over 27% in the visible light region (above 380nm). This is irrelevant with

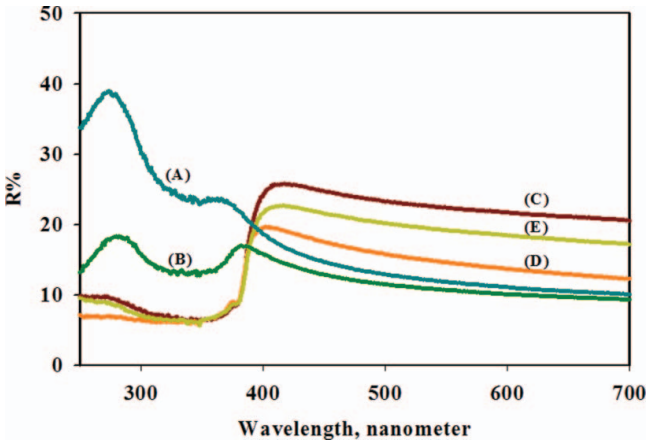

Figure 8. UV-Vis reflectance of Si-substrate, ZnO thin film, and ZnO nanorods grown by thermal evaporation method, (a) Si-substrate, (b) ZnO thin film over Si-substrate, (c) ZnO nanostructure grown with 10 wt% Zn/AC, ZnO nanostructure grown with 20 wt% Zn/AC, ZnO nanostructure grown with 30 wt% Zn/AC, (d) ZnO nanostructure grown with 20 wt% Zn/AC, (e) ZnO nanostructure grown with 30 wt% Zn/AC.

the fact that with the naked eye, single-crystalline zinc oxide appears to be white. Because the seeds maintain their polycrystalline structure, it can appear as white. As observed in SEM images, instead of the single-crystalline ZnO, the flower-like ZnO structures were formed over the substrates in the cases where 10 wt% and 30 wt% zinc acetate were loaded. Flower-like ZnO structures were not aligned well in one direction, and the polycrystalline ZnO structures were formed in the center of the flower-like structures. For these two facts, it was concluded that white is visible because of the increased polycrystalline structure, and therefore the reflectance of the visible light region could increase. Meanwhile, Fig. 9 presents the reflectance of ZnO synthesized by the wet chemical method. As shown in Fig. 9,

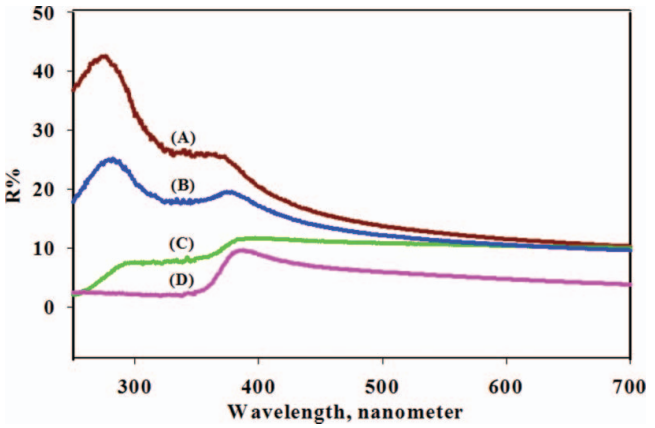

Figure 9. UV-Vis reflectance of Si-substrate, ZnO thin film, and ZnO nanorods grown by wet chemical method, (a) Si-substrate, (b) ZnO thin film, (c) ZnO nanorod grown for 1 h, ZnO nanorod grown for 2 h, (d) ZnO nanorod grown for 2 h.

the reflectance of less than 15% was observed for all wavelengths in the 400–800 nm range. The single-crystalline ZnO nanorods were exitaxially grown by the wet chemical method developed and the polycrystalline structure could not be observed because the length of the single-crystalline ZnO nanorods maintained below 100nm. They were coated on the Si substrate in their transparent state. To prevent the reflectance from such outcomes, single-crystalline ZnO nanorods for the ARC application should be epitaxially grown in the direction perpendicular to the substrate and should develop within 100nm and maintain its transparency, and lower the reflectance of visible light region.

Conclusion

ZnO nanorods for ARC application to the photovoltaic cells were epitaxially grown over the substrate using both thermal evaporation method and wet chemical method. A precursor for the thermal evaporation method was prepared by impregnating zinc acetate over the activated carbon at three different loading amounts: 10, 20, and 30 wt%. The temperature for the epitaxial growth of ZnO nanorods over the substrate was fixed to 850°C. The diameter of the synthesized single crystalline ZnO nanorods was about 1–3 μm. The shape and size of the ZnO nanorods varied with the content of the precursors loaded over the activated carbon. The length of the ZnO nanorods increased as the loading amount of the zinc was increased. Single crystalline ZnO nanorods were grown over the substrates by a hydrothermal synthesis in an autoclave reactor. Zinc nitrate was used for the precursor material in the wet chemical method. The length and diameter of the ZnO nanorods synthesized by the wet chemical method were about a few nm and 100 nm, respectively. The optical properties of ZnO nanorods, such as reflectance, were measured by the UV-Visible spectrophotometer. It was confirmed that ZnO nanorods, which is the single crystal rods of approximately 100 nm, decrease the reflectance of UV and Visible lights. Therefore, it was concluded that ZnO nanorods can be used as the antireflective material for photo voltaic cells.

Acknowledgement

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