Employing Successive Ionic Layer Adsorption and Reaction (SILAR) Method on the Fabrication of \( \text{Cu}_3\text{BiS}_3 \) - Semiconductor-Sensitized Solar Cells

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Abstract. Successive ionic layer adsorption and reaction (SILAR) method is a modified version of chemical bath deposition (CBD) that serves as a low-cost and convenient on the production of ternary metal chalcogenides. This research reported the utilization of SILAR method on the fabrication of \( \text{Cu}_3\text{BiS}_3 \) semiconductor-sensitized solar cells. The concentration of bismuth and copper precursor were varied, namely 0.03 M and 0.1 M, whereas the precursor of sulfide was varied in the concentration of 0.02 M and 0.05 M. The variation of SILAR cycles was employed to investigate the most appropriate cycle numbers in producing \( \text{Cu}_3\text{BiS}_3 \), in particular 3-9 cycles, 5-15 cycles, and 6-6 cycle with the immersing time of 20 s for each. The results show that there were only two suitable peaks appeared for 3-9 cycles and 6-6 cycles, while 5-15 cycles provide the more preferable XRD patterns with the power conversion efficiency of 0.02% (\( J_{sc} \) of 1.75 mA/cm\(^2\); \( V_{oc} \) of 0.04 V; \( F_{F} \) of 29.65%). It can be said that SILAR method with higher number of cycles can be employed to fabricate \( \text{Cu}_3\text{BiS}_3 \); however, smaller PCE came from inappropriate structure alignment between \( \text{Cu}_3\text{BiS}_3 \) and metal oxide layer.

1. Introduction

Among the methods used to synthesize ternary metal chalcogenides, successive ionic layer adsorption and reaction (SILAR) method attracts researchers’ attention recently due to its several benefits, such as its serving as an inexpensive and simple production for large area of deposition, its capacity to control the particle size of ternary metal chalcogenides by varying deposition time and number of coating cycles, its easiness to be operated at room temperature, and its flexibility in the use of the substrate [1], [2]. There are several parameters which play crucial role on the deposition process, such as immersing time, concentration of precursor solutions, and the number of cycles [1], [3]. SILAR method is successfully employed for deposition of ternary metal chalcogenides into metal oxide semiconductor to obtain tunable quantum dots, resulting large value of power energy conversion (PCE) [4]–[7].

One of ternary metal chalcogenides that has potential application on semiconductor-sensitized solar cells is copper bismuth sulfide (Cu-Bi-S) [8], [9], which was successfully used in liquid junction quantum dots-sensitized solar cells (QD-SSCs) in the form of \( \text{CuBiS}_2 \) [10] and \( \text{Cu}_2\text{BiS}_3 \) [11]. However, both researches were done by using chemical bath deposition (CBD) and solvothermal route,
respectively; therefore, the use of SILAR method to fabricate Cu$_3$BiS$_3$ should yield distinct results due to its capability to tune the particle size of deposited materials. Based on the above explanation, this study aimed to utilize SILAR method on the fabrication of Cu$_3$BiS$_3$ semiconductor-sensitized solar cells. X-Ray diffraction (XRD) pattern was provided to analyze the structure of resulted materials and PCE was obtained to figure out the effectiveness of SILAR method on the production of the assembled solar cells.

2. Materials and Method

2.1. Materials
The materials used in this study were sodium sulfide nonahydrate, bismuth nitrate, copper sulfide, DI-water, titanium dioxide paste, methanol, ethanol, FTO-glass, acetone, parafilm spacer, and polyiodide electrolyte, Pt-counter electrode.

2.2. Method
After obtaining the metal oxide (TiO$_2$) layer following the procedure of Rahayu et al. [4], the sample was immersed in the solution of bismuth nitrate precursor (varied in concentration of 0.03 M and 0.1 M) for 20 seconds, followed by rinsing by using DI-water for 25 s, dried at room temperature, and dipped into the solution of sodium sulfate precursor (varied in concentration of 0.02 M and 0.05 M) for 20 seconds, followed by rinsing in methanol and drying step. This process was called as one cycle of obtaining Bi-S particles into metal oxide layer. Subsequently, the sample was dipped into the solution of copper sulfide precursor (varied in concentration of 0.03 M and 0.1 M) for 30 s, followed by rinsing in the DI-water and drying at room temperature, and immersed into sodium sulfate precursor (varied in concentration of 0.02 M and 0.05 M) for 20 seconds followed by rinsing in methanol and drying step. This process was called as one cycle of obtaining Cu-S particles into metal oxide layer. The final step was annealing at 350º C for 50 minutes in tube furnace. The resulted photoanode was then assembled with Pt-counter electrode using parafilm spacer and filled with polyiodide electrolyte to undergo the photochemical process.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis
Figure 1 shows the X-ray diffraction pattern of Cu$_3$BiS$_3$ in the metal oxides (TiO$_2$) layer resulted by undergoing 3 cycles for Bi-S deposition and 9 cycles of Cu-S deposition. As shown, there were only two appropriate peaks of Cu$_3$BiS$_3$ resulted from SILAR method compared to Cu$_3$BiS$_3$ produced using CBD method [12], which has cell constants $a=7.697$ Å, $b=10.388$ Å, $c=6.712$ Å, having the same agreement with JCPDS card (No. 43–1479) [13]. This occurred due to the lack of deposition layer of both Bi-S and Cu-S which was obtained from 3-9 cycles.
However, when the number of cycles increased, the respectable peaks for Cu₃BiS₃ appeared more than those of 3-9 cycles as given in figure 2. It shows that the more SILAR cycles, the more peaks appeared.

This study also investigated different concentration used and order of the process as shown in figure 3. Since the concentration of precursor was increased, from 0.02 M to 0.05 M for sodium sulfate precursor and 0.03 M to 0.1 M for bismuth and copper precursor, the cycles were decreased to 6 cycles for Bi-S deposition and 6 cycles for Cu-S deposition. As seen, the appropriate peaks only existed for two positions. It gives information that for fabricating Cu₃BiS₃ using SILAR method needs large number of cycles.
3.2. Photovoltaic Measurement Results

Photovoltaic results was yielded by measuring PCE using Keithley 2400 Source Meter with Oriel 150W Xe lamp using band-pass filter simulating the AM 1.5 solar spectrum and evaluate by using the formula (1) [14]

$$PCE = \frac{FF \times I_{sc} \times V_{oc}}{P_{in}}$$  \hspace{1cm} (1)

where $I_{sc}$ is the short-circuit current, $V_{oc}$ is the open-circuit voltage, $FF$ is the fill factor, $P_{in}$ is the incident light power. $FF$ is a crucial parameter to indicate the effective output power for a solar cell as shown in the formula (2)

$$FF = \frac{P_{opt}}{I_{sc} \times V_{oc}}$$  \hspace{1cm} (2)

where $P_{opt}$ is the maximum output power.

Table 1. Photovoltaic measurement results of Cu$_3$BiS$_3$ Semiconductor-Sensitized Solar Cells

| Number of Cycles | $J$(mA/cm$^2$) | $Voc$(V) | FF(%) | PCE(%) |
|------------------|----------------|----------|-------|--------|
| 3-9              | 1.11           | 0.03     | 29.68 | 0.010  |
| 5-15             | 1.75           | 0.04     | 29.65 | 0.020  |
| 6-6 (Bi-S/Cu-S)  | 1.13           | 0.02     | 35.49 | 0.008  |
| 6-6 (Cu-S/Bi-S)  | 0.18           | 0.02     | 34.57 | 0.001  |

As given in Table 1, the cycle numbers was proved to have a huge effect of PCE; it can be seen that 5-15 cycles gave the most preferable PCE of 0.02%. However, $FF$ obtained was very low compared to 6-6 cycles. The large value of PCE of 5-15 cycles was suggested to come from the appropriate crystallinity shown in XRD pattern in Figure 2. Nevertheless, this result was much smaller than those of Yin and Jia [11] which can yield PCE of 1.281% using TiO$_2$ nanorod arrays as their metal oxide. This could occur due to different structure of metal oxide used; as mentioned that this study employed mesoporous TiO$_2$ as the structure of metal oxide, the surface to volume ratio is different from that of nanorod, resulting poor chemical reaction with the electrolyte.
4. Conclusion
To conclude, SILAR method was successfully employed to produce Cu$_3$BiS$_3$ Semiconductor-Sensitized Solar Cells with the PCE of 0.02%. The most suitable cycle number to produce such PCE was 5 cycles for Bi-S deposition and 15 cycles for Cu-S deposition, which also gave the best XRD pattern. The smaller PCE resulted from this study came from a mismatch structure of metal oxides.

5. References
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