EFFECT OF ANNEALING TEMPERATURE AND TIME ON THE PHOTOVOLTAIC PERFORMANCE OF NaSbS₂ SEMICONDUCTOR-SENSITIZED SOLAR CELLS PREPARED BY SILAR METHOD

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ABSTRACT

In the search for promising solar absorber materials, ternary metal chalcogenides, such as sodium antimony sulfide (NaSbS₂), are considered to be good candidates because of their advantages, such as easy fabrication and tunability of the bandgap. The investigation of the effect of annealing temperature and time as a post-treatment after SILAR was conducted on NaSbS₂-semiconductor-sensitized solar cells. The solar cells were prepared by assembling two main components, namely photoanode (TiO₂ as a wide gap semiconductor, NaSbS₂ semiconductor as a sensitizer, and FTO-glass as a substrate) and counter electrode (Pt). The electrolyte used in this study was polysulfide electrolyte. The results showed that from three variations of annealing temperature (350°C, 375°C, and 400°C), the temperature of 350°C gave the highest crystallinity (83.50%) and the smallest crystal size (15.26±3.05), and from three variations of annealing time (40 minutes, 50 minutes, and 60 minutes), the time of 60 minutes yielded the highest crystallinity (83.50%) and the smallest crystal size (15.26±3.05); the crystal size mentioned in this research was proved to be the same as particle size based on the TEM picture analysis. Based on these results, the best photovoltaic performance was gained from the NaSbS₂ semiconductor-sensitized solar cells prepared by annealing at 350°C for 60 minutes with the power conversion efficiency (PCE) of 2.04%. The enhancement of PCE comes from the production of electron-hole pairs, the reduced recombination rate of the cells, and the quantum effects exhibited from a more regular crystal and a smaller crystal size.

Keywords: Annealing Temperature, Annealing Time, Sodium Antimony Sulfide, Ternary Metal Chalcogenides, SILAR, Semiconductor-Sensitized Solar Cells.

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INTRODUCTION

The discovery of a new solar absorber for the application of solar cells, one of which is semiconductor-sensitized solar cells, is highly demanded.¹⁻⁵ Related to that, ternary metal chalcogenides offer many advantages as a solar absorber, such as the flexibility to tune the bandgap³, low-cost fabrication, and long carrier lifetime^{6,7}; there are much research explored the use of ternary metal chalcogenides as a solar absorber.⁸⁻¹¹

The most prominent property of ternary metal chalcogenides is their tunability of the bandgap, in which their sizes define the quantum confinement effect that influences their performance as solar absorbers.⁶ Successive ionic layer adsorption and reaction (SILAR) method is one of the most relatively convenient methods that provides the process to tune the size of ternary metal chalcogenides.¹²⁻¹⁴ In some cases, after completing the SILAR process to produce ternary metal chalcogenides, annealing is usually followed. This annealing process was found to affect their properties^{12,14,15}; for instance, Yildirim *et al.* found that higher annealing temperature yields higher current values for Cu_{0.6}Zn_{0.4}S film¹⁴; therefore, the annealing temperature and time could also have a relation to the size of yielded ternary metal chalcogenides.

One of the ternary metal chalcogenides that are very promising to be used as a solar absorber is NaSbS₂, which was first utilized as a solar absorber by using the SILAR method; this material resulted in an efficiency of 3.18% under 0.1 sun in the form of liquid junction semiconductor-sensitized solar cells.¹⁶ Similarly, Sun *et al.* also reported that the efficiency of 4.11% came from NaSbS₂-quantum dots-sensitized solar cells that were fabricated by employing the SILAR method. Both studies used an annealing process after SILAR was complete.¹⁷ In fact, Xia *et al.* reported that there was a phase transition from cubic to the monoclinic structure of NaSbS₂ produced by spray-pyrolysis method when the annealing temperature increased¹⁸; the mentioned research open the question on how the annealing temperature and time contribute to the photovoltaic performance of NaSbS₂ semiconductor-sensitized solar cells (NaSbS₂ semiconductor-SSCs) prepared by SILAR method. NaSbS₂ itself has been studied to possess promising photoelectric and optical properties; it has an absorption coefficient of 10⁴ cm⁻¹ to 10⁵ cm⁻¹ in the visible light range and bandgap value of 1.5 eV to 1.8 eV that came from experimental results.^{19,20} Besides, the element involved in the production of NaSbS₂ are abundant and environmentally friendly²¹, so the investigation of NaSbS₂ is worth to be studied further.

Even though the study about NaSbS₂ on solar cells has expanded theoretically and experimentally using many types of methods other than SILAR^{20,22,23}, to our best knowledge, there are limited reports about how the annealing temperature and time affect the photovoltaic performance of NaSbS₂ produced by using the SILAR method; therefore, this research aimed to investigate the effect of annealing temperature and time on the photovoltaic performance of NaSbS₂ semiconductor-SSCs. The characterizations involved in this study are XRD pattern, photovoltaic measurement results, and transmission electron microscopy (TEM) pictures.

EXPERIMENTAL

Materials

This study used the following materials: antimony trichloride (99.9%, Alfa Aesar), sulfide nonahydrate (≥98%, Acros Organics), methanol (99.5%, Macron Fine Chemicals), ethanol (99.5%, ECHO), titanium dioxide screen print paste TSL-IP-T/40 nm (Taiwan DSC PV), titanium dioxide WER4-O (Dyesol), titanium (IV) isopropoxide (98+%, ACROS), FTO glass substrate (15Ω/sq, Nippon Sheet Glass), sulfur powder (99%, SHOWA), sodium hydroxide (>95%, Shimakyu's Pure Chemicals), potassium chloride (>98%, Choneye Pure Chemicals), potassium iodide (99.5%, Shimakyu's Pure Chemicals), parafilm sheet (130 μm, Pechiney).

Method

In this research, the structure of the assembled NaSbS₂-semiconductor-sensitized solar cells were photoanode with FTO-glass as substrate (0.05-0.07 μm thick of TiO₂ blocking layer, 10 μm thick of NaSbS₂-coated mesoporous TiO₂, and 5 μm thick of TiO₂ scattering layer); Pt counter electrode, which was deposited on FTO-glass; and polysulfide electrolyte (0.25M of Na₂S, 1M of S, 0.2M of KCl, 0.1M of KI, methanol/water (7:3 by volume)). The assembly of NaSbS₂-semiconductor-sensitized solar cells was done by employing a parafilm spacer with a thickness of 190 μm. The I-V curve from assembled cells was obtained from a Keithley 2400 Source Meter with the light generated by Oriel 150 W Xe lamp using band-pass filter simulating (100 mW/cm²)

In order to grow NaSbS₂ onto mesoporous TiO₂, the SILAR method was applied, as explained by Rahayu *et al.* (2016) and Sun *et al.* (2018).^{16,17} In brief, the non-coated photoanode underwent 15 s of immersion in a 0.1 M of SbCl₃ ethanol solution; then, it was rinsed in ethanol and dried in air. This process resulted in Sb³⁺ ions-coated mesoporous TiO₂, which was directly dipped into a solution of 0.1 M Na₂S in methanol for 1 minute. The rinsing in methanol and drying step follows afterward, obtaining S²⁻ ions adsorb by Sb³⁺ ions-coated mesoporous TiO₂. These two immersion processes were repeated for 11 cycles. The illustration of the SILAR process applied in this study was given in Fig.-1, while the reaction depicted in Fig.-1 was based on an explanation by Sun *et al.* (2018).¹⁷

The post-treatment was annealing; in this study, the annealing temperature was varied, namely 350°C, 375°C, and 400°C; the duration of annealing was 60 minutes. In addition, the annealing time was also diversified for the best annealing temperature (350°C), in particular, 40 minutes, 50 minutes, and 60 minutes.

In obtaining XRD patterns, the NaSbS₂-coated mesoporous TiO₂ was deposited on top of FTO glass and measured by PANalytical X'Pert Pro MRD diffractometer, while the TEM pictures were obtained from JEOL JEM 2010.

Fig.1-Schematic illustration of SILAR method in obtaining NaSbS₂-coated mesoporous TiO₂

RESULTS AND DISCUSSION

Based on the fact that the potentiality of NaSbS₂ to be a sensitizer for solar cells was unexpectedly found in the process of synthesizing another ternary metal chalcogenides that used Na₂S as a sulfur source, namely Ag₃SbS₃^{16,24}; the annealing temperature of synthesizing Ag₃SbS₃ was followed, namely 375°C. In order to investigate the effect of annealing temperature, the study was then expanded to a higher annealing temperature (400°C) and to a lower annealing temperature (350°C).

Figure-2 shows the comparison of XRD patterns under different annealing temperatures. It can be seen that all major peaks contributed to the NaSbS₂ (JCPDS number of 00-032-1039), TiO₂, and SnO₂ (as a substrate), there is no impurity in the resulting pattern. The formed NaSbS₂ has a monoclinic structure that is a stable structure.^{25,26}

Fig.-2: XRD Patterns of NaSbS₂-coated mesoporous TiO₂ under different annealing temperatures

The crystallinity of NaSbS₂-coated mesoporous TiO₂ with FTO-glass as a substrate was calculated by using Origin software, in which the crystallinity refers to peak to noise ratio based on the formula given in equation (1); Table 1 gives the calculated results.

$$\text{Crystallinity} = \frac{\text{Area of Crystalline peaks}}{\text{Area of all peaks}} \times 100\% \quad (1)$$

Table-1: Crystallinity of NaSbS₂-coated mesoporous TiO₂ with FTO-glass as a Substrate

No	Annealing Temperature	Crystallinity
1	350°C	83.50%
2	375°C	78.97%
3	400°C	69.51%

Based on the intensity of peaks depicted in Fig.2 and the calculation of crystallinity in Table-1, the annealing temperature of 350°C gave higher crystallinity (83.50%) compared to that of 375°C (78.97%) and 400°C (69.51%); higher annealing temperature gave lower crystallinity which also refers to the arrangement of atoms in the lattice. In the case of TiO₂, well-crystallized TiO₂ has a lower recombination rate of electron-hole pairs²⁷⁻²⁹; NaSbS₂, which is also a semiconductor, could exhibit the same electronic property. Besides, the regular arrangement of atoms in the lattice could result in a single value of work function, increasing electron-hole pair production with only a small applied voltage. Therefore, better photovoltaic performance was hoped to come from the sample with higher crystallinity.

In addition, the crystal size of NaSbS₂ was calculated from the XRD pattern by using the Scherrer formula given in equation (2); Table-2 depicts the calculated results.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

From equation (2), D is particle size, λ is the X-ray wavelength (1.54 Å), k is Scherrer constant (0.9), β is the width of the peak in radian, and θ is the angle of the peak.

Table-2: The Crystal Sizes of NaSbS₂-coated mesoporous TiO₂ under different annealing temperatures

No	Miller Indices	Crystal Size (nm)		
		350°C	375°C	400°C
1	(1 1 0)	15.84	17.49	28.95
2	(-2 2 1)	11.96	17.94	18.32
3	(0 0 2)	17.98	19.62	21.58
Average Crystal Size		15.26±3.05	18.35±1.12	22.95±5.44

As shown in Table-2, the average crystal size of the NaSbS₂-coated mesoporous TiO₂ annealed at 350°C was the smallest of all (15.26±3.05 nm). Related to crystal size, the TEM pictures shown in Fig.-3 depict that the crystal or grain size is the same as particle size so that the resulting NaSbS₂ could be said to be in a quantum dot state. The size of quantum dots has relation to the increase of energy gap, and smaller quantum dots have more advantageous from the quantum effects than those of larger particles^{30,31}; therefore, the NaSbS₂-coated mesoporous TiO₂ annealed at 350°C was expected to undergo better performance.

Fig.3- TEM Pictures of (a) Bare TiO₂ and (b) NaSbS₂-coated mesoporous TiO₂ (the arrow shows the quantum dots of NaSbS₂)

To further examine the effect of the crystallinity and the crystal size of the resulting NaSbS₂, the photovoltaic measurement was conducted, and the results are in agreement with the analysis of XRD

patterns, which shows that the best power conversion efficiency (PCE) was yielded at an annealing temperature of 350°C, which has the highest crystallinity and the smallest crystal size, with PCE of 2.04% with V_{oc} of 0.43 V and J_{sc} of 11.22 mA/cm² as shown in Fig.-4 and Table-3. As the annealing temperature increased, the performance of NaSbS₂-semiconductor-sensitized solar cells decreased; higher temperature during the annealing process gave less regular arrangement of atoms (lower crystallinity), yielding lower V_{oc} and J_{sc} at the cell annealed at 400°C with only 0.40 V of V_{oc} and 4.31 of J_{sc} , while the cells annealed at 375°C has lower J_{sc} and FF . These lower photovoltaic performances might occur due to the higher recombination rate of electron-hole pairs and lower production of electron-hole pairs, as mentioned as the results of the lower crystallinity. This result is in agreement with the study by Rahayu *et al.* (2016), which mentioned that the best annealing temperature in fabricating NaSbS₂-semiconductor sensitized solar cells was 350°C²¹. Besides, smaller crystal size, which exhibits more subtle quantum effects^{30,31}, also contributes to the performance of the cells.

Fig.-4: I - V Curves of NaSbS₂-semiconductor sensitized solar cells under different annealing temperatures

Table-3: Photovoltaic Performance of NaSbS₂-semiconductor sensitized Solar Cells under different annealing temperatures

No	Annealing Temperature	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
1	350°C	11.22	0.43	42.25	2.04
2	375°C	9.14	0.43	38.73	1.52
3	400°C	4.31	0.40	42.71	0.736

In order to investigate the effect of annealing time on the photovoltaic performance of NaSbS₂-semiconductor sensitized solar cells, the annealing time was varied at the best annealing temperature (350°C). Figure-5 shows the comparison of XRD patterns of NaSbS₂-coated mesoporous TiO₂ annealed at 350°C under different annealing times; all peaks contributed to NaSbS₂, TiO₂ and SnO₂ (as a substrate); no impurities were detected on the patterns.

Fig.-5: XRD Patterns of NaSbS₂-coated mesoporous TiO₂ annealed at 350°C under different annealing time

As depicted in Fig.-4, the intensity of the sample annealed at 350°C for 60 minutes has the highest intensity of all prepared samples. The crystallinity of NaSbS₂-coated mesoporous TiO₂ with FTO-glass as a substrate was calculated by using equation (1); Table 4 gives the calculated results.

Table-4: Crystallinity of NaSbS₂-coated mesoporous TiO₂ annealed at 350°C with FTO-glass as a substrate

Annealing Time	Crystallinity
40 minutes	76.44%
50 minutes	69.70%
60 minutes	83.50%

Based on Table-3, the largest crystallinity of NaSbS₂-coated mesoporous TiO₂ with FTO-glass as a substrate annealed at 350°C was achieved with the annealing time of 60 minutes (83.50%), while the smallest crystallinity came from 50 minutes of annealing time with only 69.70%. It indicates that 60 minutes gave sufficient time for the particles of NaSbS₂ deposited by SILAR to arrange themselves in a corresponding lattice. As also can be seen from Table-4, the crystallinity of the sample annealed for 40 minutes is higher than that of 50 minutes; it can be assumed that while the particles of NaSbS₂ grow during the annealing process, the arrangement of those particles improves until 40 minutes. When the time rises to 50 minutes, the arrangement of the particles changes, resulting in smaller crystallinity, and eventually gains better crystal perfection when the annealing time increases to 60 minutes.

The crystal size of NaSbS₂-coated mesoporous TiO₂, which is the same as its particle size, was also measured by using Scherrer formula given in equation (2); the results were given in Table-5. As can be seen, the smallest particle size was from the sample annealed at 350°C for 60 minutes (15.26±3.05 nm); this indicates that there are the more strong quantum effects undergo in the NaSbS₂-semiconductor sensitized solar cells prepared at 350°C for 60 minutes, resulting in better photovoltaic performance.

Table-5: The Crystal Sizes of NaSbS₂-coated mesoporous TiO₂ under different annealing time

No	Miller Indices	Particle Size (nm)		
		40 minutes	50 minutes	60 minutes
1	(1 1 0)	18.72	16.88	11.96
2	(-2 2 1)	15.98	17.62	17.98
3	(0 0 2)	18.25	18.66	15.84
Average Crystal Size		17.65±1.46	17.72±0.89	15.26±3.05

The photovoltaic measurement results given in Fig.-6 and Table-6 also show that the best photovoltaic performance was given by the cells prepared with 60 minutes of annealing process with PCE of 2.04%. The substantial difference was in fill factor (*FF*) of the cells, which has relation with the shunt and series resistance of equivalent circuit of the prepared cells, in which the loss of *FF* in the cells prepared by annealing 50 minutes was contributed from the series resistance of equivalent solar cells circuit.³²

Fig.-6: *I-V* Curves of NaSbS₂-semiconductor sensitized solar cells under different annealing time

Table-6: Photovoltaic Measurement Results of NaSbS₂-semiconductor sensitized Solar Cells under different annealing time

No	Annealing Time	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	$FF(\%)$	$PCE(\%)$
1	40 minutes	11.36	0.44	40.35	2.02
2	50 minutes	10.34	0.44	36.67	1.67
3	60 minutes	11.22	0.43	42.25	2.04

CONCLUSION

In summary, the annealing temperature and time were investigated to affect the photovoltaic performance of NaSbS₂-semiconductor sensitized solar cells. The cells prepared with an annealing temperature of 350°C for 60 minutes show the best photovoltaic performance with a PCE of 2.04%. It can be explained that the regular arrangement of atoms during the annealing process contributed to the production of electron-hole pairs as well as the recombination rate of the cells. The smaller crystal size, which refers to particle size, contributes to being more advantageous to the performance of NaSbS₂-semiconductor sensitized solar cells due to the quantum effects.

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