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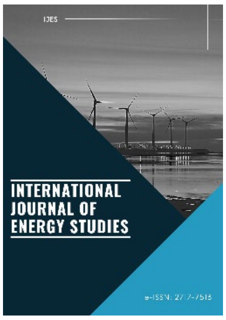

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Correlation between silver alloying, post-deposition treatment, and photovoltaic parameters in chalcopyrite thin film solar cells produced at low temperature

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Highlights

- CIGSe thin film solar cells were produced with and without silver alloying and post-deposition treatment at low temperature.
- Silver alloying increased the average grain size, the solubility of the sodium, the current collection, and the efficiency of the solar cells.
- Post-deposition treatment increased the photovoltaic parameters of the solar cells.
- The power conversion efficiency of the reference solar cell was successfully increased from 12.9% to 16.2% by application of both silver alloying and post-deposition treatment.

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ABSTRACT

In this study, the correlation between silver alloying, post-deposition treatment, and photovoltaic parameters in chalcopyrite thin film solar cells produced by multi source physical vapour deposition chamber at low temperature was investigated by scanning electron microscope, energy dispersive X-ray spectroscopy, glow discharge optical emission spectroscopy, current density-voltage, and external quantum efficiency measurement techniques. It is found that, the silver alloying increased the average grain size in samples with and without NaF post-deposition treatment while NaF post-deposition treatment did not have a significant effect on average grain size. Silver alloying did not have an important effect on open circuit voltage without NaF post-deposition treatment application. However, NaF post-deposition treatment increased the open circuit voltage value of the reference sample from 598 mV to 628 mV. Moreover, the application of both silver alloying and NaF post-deposition treatment resulted the best open circuit voltage with 658 mV. Both the application of silver alloying and NaF post-deposition treatment separately and the application of both together improved the fill factor and short circuit current density values. The distributions of gallium and indium in the samples became more homogeneous and the solubility of the sodium in the structure was increased after silver alloying. Post-deposition treatment decreased the open circuit voltage deficit and both NaF post-deposition treatment and silver alloying improved the solar cell efficiency. The best efficiency of 16.2% was obtained in the sample with silver alloying and the NaF post-deposition treatment.

Keywords: Silver alloying, Solar cell, Low temperature, Post-deposition treatment

1. INTRODUCTION

Copper indium gallium selenide (CIGSe) solar cells consist of substrate, back contact, absorber, buffer layer, window layer, transparent conductive oxide layer, and front contact. Although each layer has its own importance for highly efficient solar cell production, the absorber layer has attracted much more attention. The most important reasons for choosing CIGSe thin film as an absorber are tunable bandgap, high absorption coefficient, high efficiency, stability, and low cost with effective usage of raw materials [1-9]. When CIGSe and crystalline silicon solar cells, whose maximum efficiency values are close to each other, are compared, it is seen that the properties of CIGSe solar cells, such as energy payback time and energy return on energy invested, are better than crystalline silicon solar cells [10]. Another important feature of CIGSe solar cells compared to crystalline silicon solar cells is that both the bandgap and the bandgap depth profile can be adjusted [11-13].

In recent years, there has been an increase in silver alloying in CIGSe solar cell studies, where silver partially or completely replaces the copper in the structure. The main motivations for this increase are that the thermal budget decreases as the melting temperature of the composition decreases after silver alloying, and the crystal quality increases and the solar cell efficiency increases by reducing defects in the structure [14-16]. Additionally, there are studies in the literature in which the bandgap is widened and the open circuit voltage (Voc) is increased by silver alloying [17-19]. However, excessive silver alloying can also bring about negative consequences such as microstrain, increase in defects, increase in carrier recombination rate and decrease in Voc [20]. Extensive research on samples with different silver alloying ratios has revealed that for narrow bandgap chalcopyrite solar cells with a bandgap of approximately 1.1 eV, an Ag/(Ag+Cu) ratio of 0.2 is very beneficial to the efficiency of the solar cell [21].

There are also important studies on the effect of adding alkaline elements on the power conversion efficiency (PCE) of silver alloyed CIGSe solar cells [22-24]. Alkaline element addition can be done in three different ways; pre-deposition, during co-evaporation, and post-deposition. Post-deposition treatment (PDT) is more advantageous than other methods as it passivates defects without affecting crystal quality and improves the electrical properties of the solar cell [25]. Although PDT has positive effects, it should be taken into consideration that the addition of excessive alkali will also create a new surface due to precipitates, which will seriously reduce the photovoltaic properties of the solar cell [26].

In order to produce high-efficiency CIGSe solar cells, the substrate temperature must be increased to high temperatures, which increases production costs. When the substrate temperature is lowered to reduce the thermal budget, alkaline element solubility may decrease. With silver alloying, high efficiency solar cell production at low temperatures can be made possible by both lowering the melting temperature of the alloy and increasing its alkali solubility [27]. In this study, the correlation between silver alloying, PDT, and photovoltaic parameters in chalcopyrite thin film solar cells produced at low temperature was investigated by electrical and structural characterization methods. It is aimed to reduce the thermal budget and therefore production costs by producing highly efficient solar cells at lower temperatures.

2. EXPERIMENTAL DETAILS

Production of the solar cells consists of molybdenum coated glass supply, p-type silver alloyed and unalloyed absorber layer coating, optional application of NaF PDT, n-type CdS buffer layer coating, undoped ZnO window layer deposition, indium tin oxide (ITO) transparent conductive oxide (TCO) layer coating for lateral conductivity and deposition of front contact by mask application steps. Only the chemical composition of the absorber layer and the PDT application state were changed, other parameters were kept constant. The two microns thick absorber layer and 6 nm thick PDT depositions were realized by a multi source physical vapour deposition chamber at 420 °C. The CIGSe reference sample without silver alloying and without PDT was named “R”. The sample with silver alloying and without PDT was named “R+Ag”. The sample without silver alloying and with PDT was named “R+NaF”. Finally, the sample with silver alloying and PDT was named “R+Ag+NaF”.

Microstructure photos of the absorber layers were taken by scanning electron micrscope (SEM) with an acceleration voltage of 5 kV. The acceleration voltage was increased to 15 kV in energy dispersive X-ray spectroscopy (EDS) measurements to be able to get compositional information through all the thickness. Compositional depth profiles of samples were analyzed by glow discharge optical emission spectroscopy (GDOES). The photovoltaic parameters of the fill factor (FF) and the Voc were determined by current density-voltage (J-V) measurement. The short circuit current density (Jsc) and bandgap values were obtained using external quantum efficiency (EQE) measurement. J-V and EQE measurements were realized under AM1.5G standard test conditions at room temperature.

3. RESULTS AND DISCUSSION

The results of the EDS measurements of the absorber layers produced by multi source physical vapour deposition chamber are shown in Table 1.

Table 1. EDS measurement results of the absorber layers

Sample	**Element (at. %)**				
	Ag	**Cu**	**In**	**Ga**	**Se**
R	---	24.2	20.6	5.9	49.3
R+Ag	4.5	19.4	20.1	5.8	50.2
R+NaF	---	23.4	19.1	5.5	52.0
R+Ag+NaF	4.7	18.7	19.5	5.6	51.5

It can be seen from Table 1 that, In, Ga, and Se amounts of each sample were very close to each other. Furthermore, the total Ag and Cu amounts (Ag+Cu) of samples were also comparable. This shows that the reproducibility level of the production system is quite good. It can be calculated from Table 1 that, all samples have (Ag+Cu)/(Ga+In) and Ga/(Ga+In) ratios of 0.9 and 0.2, respectively. While the (Ag+Cu)/(Ga+In) ratio of 0.9 is compatible with other studies [9], the Ga/(Ga+In) ratio of 0.2 shows that the amount of gallium in the structure is less compared to other studies with a ratio of 0.3 [28]. Since it is known that both low substrate temperature and high gallium amount negatively affect diffusion mechanisms [29], the negative effect that may occur due to low temperature has been tried to be minimized by intentionally reducing the amount of gallium. Ag/(Ag+Cu) ratios of R+Ag and R+Ag+NaF samples were found to be 0.2 which is the desired ratio for solar cells with a narrow bandgap [21].

The bandgap values of the samples were calculated using the point where the 20% value of the normalized EQE intersects the EQE-Wavelength graph in the high wavelength region. According to these calculations, the bandgaps of samples R, R+Ag, R+NaF, and R+Ag+NaF were found to be 1.06 eV, 1.09 eV, 1.07 eV, and 1.09 eV, respectively. It was determined that all samples had a narrow bandgap structure. Although NaF PDT does not have a significant effect on the bandgap, it can be said that silver alloying slightly increases the bandgap and this is in agreement with the literature [18]. Microstructure photos of the absorber layers are shown in Figure 1.

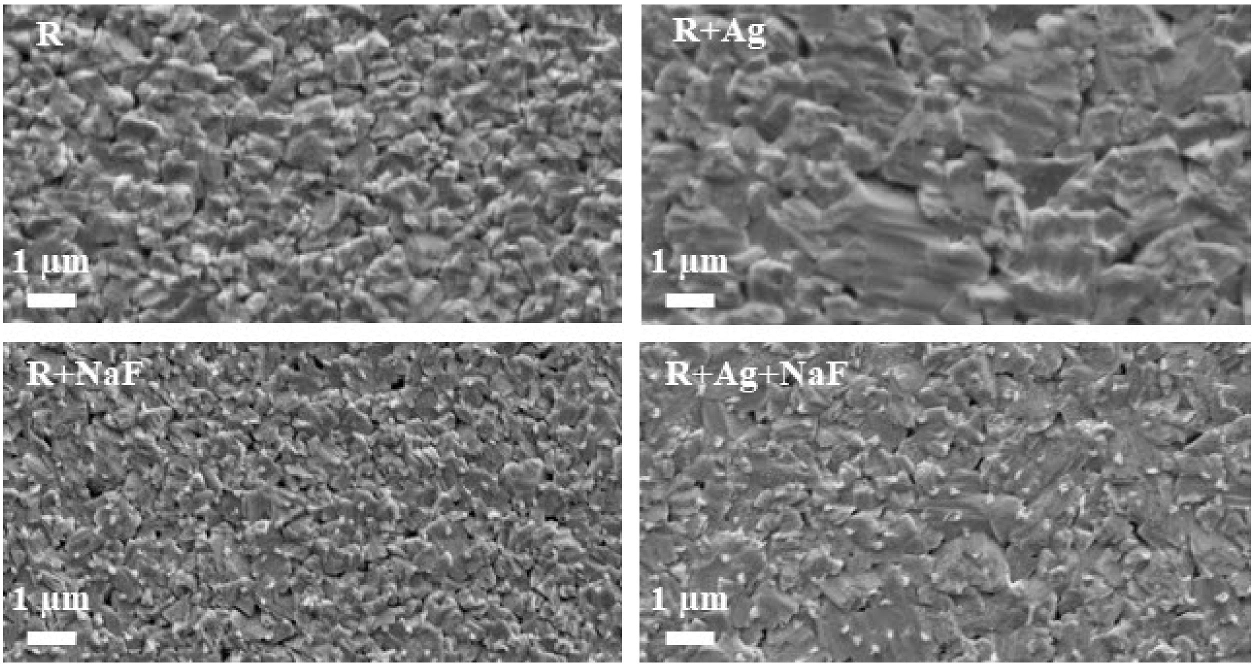

Figure 1. Microstructure photos of the absorber layers

Figure 1 shows that, small white particles formed on the surface of samples to which NaF PDT was applied. It is clear from Figure 1 that, silver alloying increased the average grain size in samples with and without NaF PDT. This situation is in a good agreement with the literature and is explained by the mechanism of facilitating the movement of atoms and grain boundaries as the melting temperature of the chalcopyrite compound decreases [20]. It was also observed that NaF PDT did not have a significant effect on average grain size. J-V and EQE measurement results are shown in Figure 2.

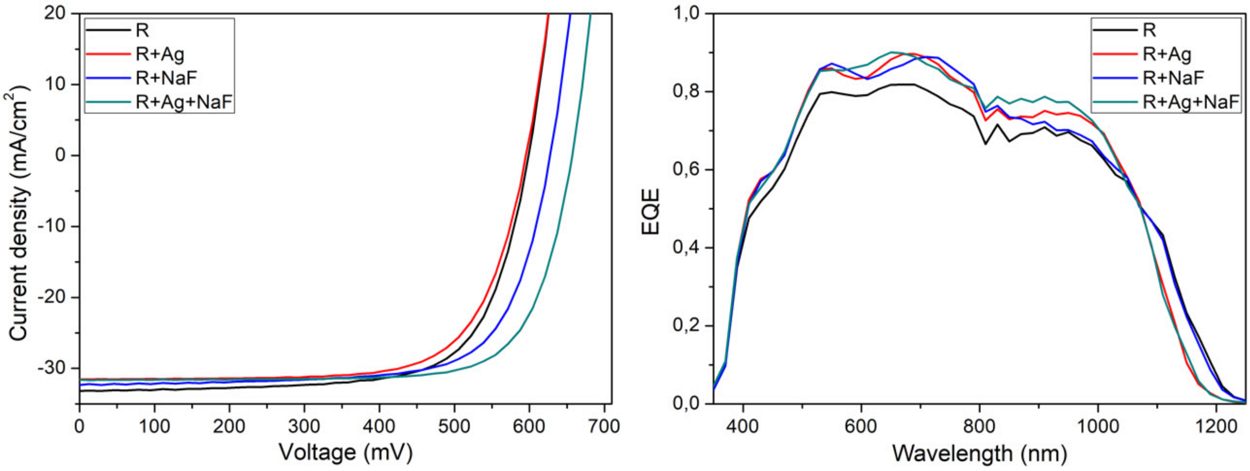

Figure 2. J-V and EQE measurement results of the samples

J-V measurement results showed that, Voc values of sample R and R+Ag were very close to each other with 598 mV and 596 mV, respectively. As a result, silver alloying did not have a significant effect on Voc when NaF PDT was not applied. When the sample R was compared with the sample R+NaF, it was seen that NaF PDT significantly increased the Voc value to 628 mV. When the sample R+NaF was compared with the sample R+Ag+NaF, it can be said that silver alloying significantly improved the Voc value by increasing it to 658 mV, unlike the situation where NaF PDT was not applied. This was thought to be due to the fact that silver alloying increases the solubility of NaF [27]. On the other hand, both silver alloying and NaF PDT had a positive effect on the FF value. The FF values of samples R, R+Ag, R+NaF, and R+Ag+NaF were found to be 70, 71, 72, and 75, respectively. The improvement in the FF value with silver alloying can be explained by the fact that the grain boundaries decrease as a result of the increase in the average grain size, and thus the defects that may occur at the grain boundaries decrease [30]. Moreover, it is thought that the increase in FF value as a result of NaF PDT application is related to the decrease in carrier recombination [31].

It can be seen in Figure 2 that, the silver alloying and the NaF PDT increased the current collection up to a wavelength of 1100 nm. The slightly decrease in the current collection after the 1100 nm wavelength was thought to be due to the increase in the bandgap, which allows current to be collected from a more limited part of the solar spectrum. It was determined that the best current collection was in the sample R+Ag+NaF. Furthermore, the Jsc value which was calculated by the integration of the EQE results with the AM1.5G solar spectrum was improved by both silver alloying and the application of NaF PDT. Jsc values of the samples, which are also related to the current collection, were calculated as 30.6 mA, 32.4 mA, 32.5 mA, and 32.7 mA for R, R+Ag, R+NaF, and R+Ag+NaF, respectively. The best current collection and the highest Jsc value were obtained in the sample with both silver alloying and NaF PDT applied. The increase in Jcs with silver alloying and NaF PDT can be attributed to the faster extraction and transfer of the holes with a decrease in parasitic optical losses [11].

The effect of silver alloying on the distribution of sodium and other elements through the depth of the samples was shown by the GDOES measurement results in Figure 3. Sodium, copper, and silver distributions were shown by elemental percentages, while those of gallium and indium were shown by the Ga/(Ga+In) ratio.

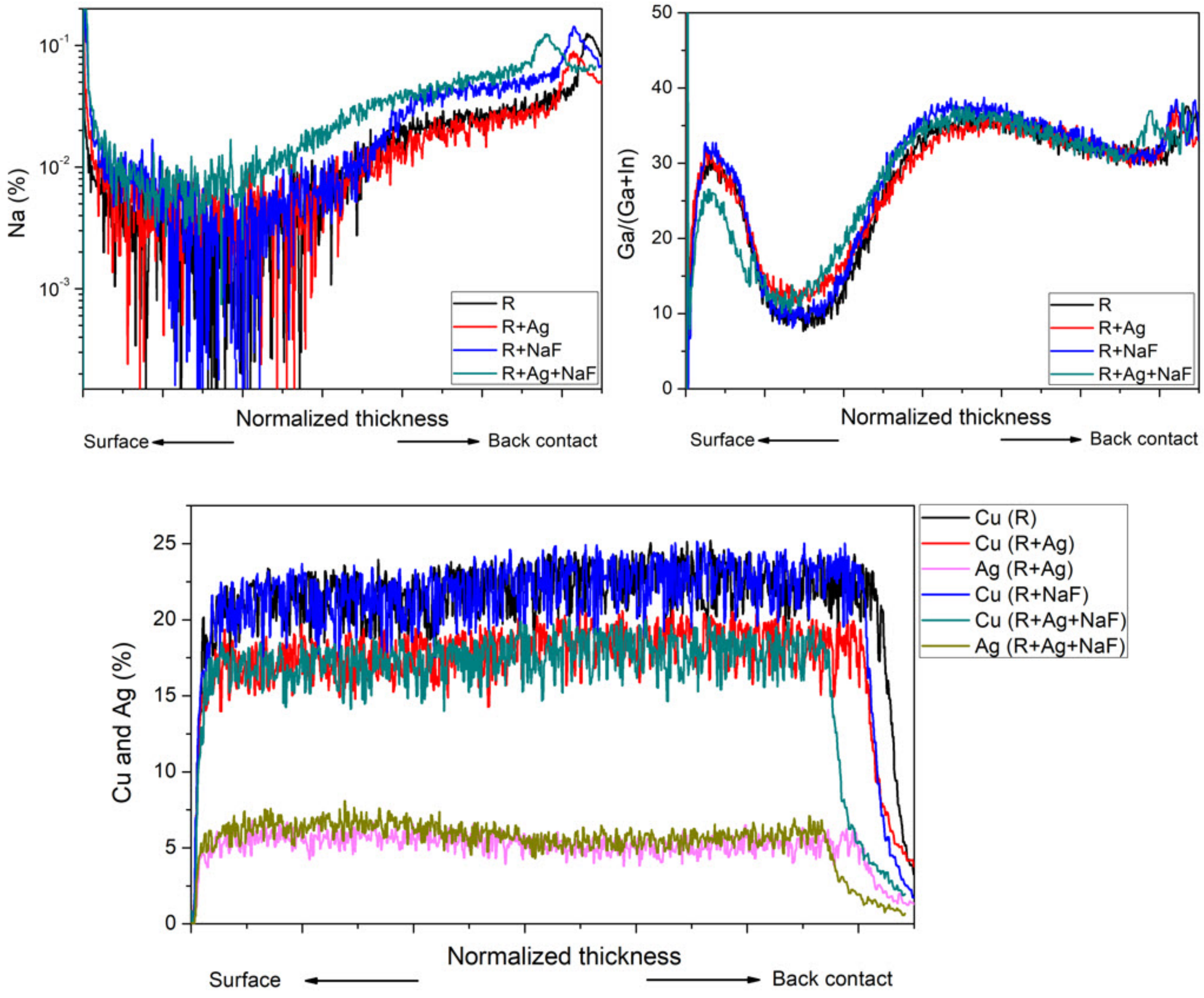

Figure 3. GDOES measurement results of the samples

According to GDOES measurement results, the copper and silver distributions of the samples were quite homogeneous. Ga/(Ga+In) depth profile graph shows that, the amount of gallium was higher close to surface and near the back contact for all samples. On the other hand, the amount of indium was higher close to middle region of the samples. Ga/(Ga+In) distributions of all samples were close to each other through all the thickness. However, it can be said that a better distribution was achieved by moving the notch in the distribution of the Ga/(Ga+In) ratio of silver alloyed samples slightly higher. This may be due to better crystal quality and easier diffusion after the silver alloying [14].

All samples contain sodium coming from the substrate with diffusion. However, in the R+NaF and R+Ag+NaF samples, sodium was also added via NaF PDT. It can be seen from Figure 3 that, the total amount of sodium in NaF PDT applied samples was higher than the ones without PDT.

Moreover, when the sodium depth profiles of silver alloyed and unalloyed samples were compared, it was seen that the sodium distributions of silver alloyed samples were more homogeneous than the unalloyed ones. This result confirms the information in the literature that silver alloying increases alkali solubility [27]. The photovoltaic parameters, Voc deficit, and bandgap values of the samples are shown in Figure 4.

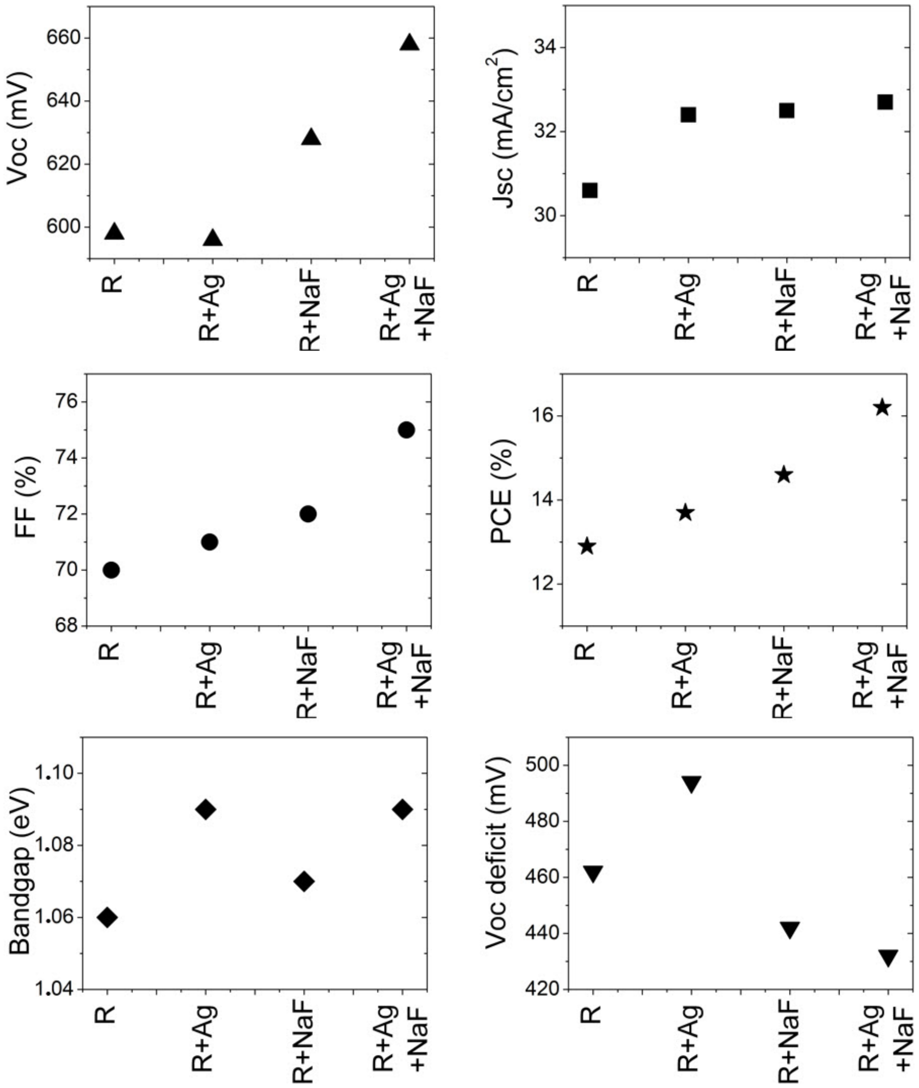

Figure 4. Photovoltaic parameters, Voc deficit, and bandgap values of the samples

PCE values were calculated using Voc, Jsc, and FF values, and Voc deficit values were calculated from the difference between the bandgap and Voc. It is clear from Figure 4 that, the Voc deficit decreased after the NaF PDT application by reducing the electrical losses. Compared to the reference sample with a Voc deficit value of 462 mV, this value could be reduced to 432 mV in the silver alloyed and NaF PDT applied sample.

Voc deficit values of R+Ag and R+NaF samples were calculated as 494 mV and 442 mV, respectively. Silver alloying increased the efficiency value of the reference solar cell from 12.9% to 13.7%, while NaF PDT increased the efficiency value of the reference solar cell to 14.6%. Finally, the best efficiency value of 16.2% was obtained in the solar cell where silver alloying and NaF PDT were applied together.

4. CONCLUSION

The correlation between silver alloying, PDT, and photovoltaic parameters in chalcopyrite thin film solar cells produced by multi source physical vapour deposition chamber at low temperature was investigated by SEM, EDS, GDOES, J-V, and EQE measurement techniques. According to the results, the reproducibility level of the production system is quite good and can be used for producing highly efficient thin film solar cells. While NaF PDT did not have a significant effect on the bandgap, silver alloying slightly increased it. Silver alloying increased the average grain size in samples with and without NaF PDT. On the other hand, NaF PDT did not have a significant effect on average grain size. Silver alloying did not have a significant effect on Voc without NaF PDT application. However, NaF PDT increased the Voc value of the reference sample from 598 mV to 628 mV. Moreover, the application of both silver alloying and NaF PDT resulted the best Voc with 658 mV. Silver alloying, NaF PDT, and the application of both together increased the FF and Jsc values separately. Gallium and indium distributions of the samples became more homogeneous after silver alloying and it increased the solubility of the NaF in the structure. NaF PDT decreased the Voc deficit and both NaF PDT and silver alloying improved the solar cell efficiency. The best efficiency of 16.2% was obtained in the sample with silver alloying and the NaF PDT. The negative effects of low temperatures were suppressed by silver alloying and NaF PDT application, and thermal budget and production costs were reduced by producing highly efficient solar cells at low temperatures.

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DECLARATION OF ETHICAL STANDARDS

The author of the paper submitted declares that nothing which is necessary for achieving the paper requires ethical committee and/or legal-special permissions.

CONTRIBUTION OF THE AUTHORS

Semih Ağca: Performing the experiments and analyzing the results, writing the manuscript.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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