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Removal of CuS phases from electrodeposited $CuInS_2$ films

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Abstract

CuS phases degrade the performance of electrodeposited and sulfurized $CuInS_2$ films acting as absorption layers for solar cell applications. In this study, CuS phases have been effectively removed from $CuInS_2$ films by using a two-stage thermal treatment and electrochemical etching. Multiple material analyses, including X-ray diffraction, scanning electron microscopy, and energy-dispersive spectroscopy, were performed to examine the presence of CuS on $CuInS_2$ films. Results indicate that sulfurization with a two-stage thermal treatment enables sulfur atoms to distribute uniformly, thereby enhancing a full reaction between the CuIn precursor film and the sulfur powder. Additionally, electrochemical etching provides an alternative method to eliminate CuS phases in a low-temperature process.

Keywords: $CuInS_2$; CuS; 2-stage thermal treatment; Electrochemical etching; Electro-deposition

1. Introduction

Solar cells have been intensively studied as an alternative energy source. Many manufacturers who fabricate solar cells have recently replaced traditional silicon with compound materials, more capable of efficiently converting sunlight into electricity. Of these type of solar cells, $CuInS_2$ or $CuInSe_2$ (CIS) can attain a light absorption rate above $10^5\ cm^{-1}$. In particular, $CuInS_2$ thin films have a non-toxic fabrication process and a desirable band gap of 1.5 eV, approaching the most appropriate range for high photovoltaic conversion. Using these thin films for the absorption layer of solar cells have attracted growing attention from polycrystalline ternary semiconductors [1] due to its wide band gap, high absorption coefficient, broad spectrum absorption, and high thermal stability.

Various techniques have been proposed to synthesize high-quality $CuInS_2$ films, including molecular beam epitaxy [2], sputtering [3], evaporation [4], and atomic layer deposition [5]. In contrast to these expensive vacuum fabrication methods, wet processes such as pyrolysis [6] and electrodeposition [7] have also been investigated. A two-step CIS film fabrication process made up of electrodeposition and sulfurization show promise as an alternative method for growing high-quality films because of its low cost, rapid production, and large-area fabrication [8,9]. However, redundant crystalline phases other than $CuInS_2$ can be introduced during the electrochemical deposition process. Specifically, impurities such as CuS phases in the absorption layer can function as electron–hole recombination centers [10], degrading the solar cell. Eliminating excessive impurities is crucial to optimize the CIS film quality and and enhance solar cell performance. In this research, non-toxic thermal and electrochemical treatments have been shown to replace toxic KCN to remove CuS complex phases in preparing $CuInS_2$ films [11]. Two methods, sulfurization with a two-stage heat treatment and electrochemical etching, are proposed to effectively suppress CuS phases from electro-deposited $CuInS_2$ films. This two-stage thermal treatment has been intensively explored for the fabrication of carbon nanotubes [12,13], and has been used to induce the appropriate distribution of sulfur atoms before sulfurization. These studies

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indicate that CuS phases can be mitigated, and high-quality $CuInS_2$ films can be produced. Furthermore, studies have also shown that carbon impurities have been effectively removed from diamond film using a KOH electrochemical etching technique without damaging the deposited film [14]. This same technique was used to eliminate CuS impurities from $CuInS_2$ films. These two CuS removal techniques [15,16] were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS) to examine the material properties of the $CuInS_2$ film and the presence of CuS.

2. Experimental Method

To investigate the elimination of CuS from $CuInS_2$ film, Cu–In alloys were first deposited using an electrodeposition system consisting of two electrodes: Pt for the counter electrode and indium tin oxide (ITO) for the working electrode with an AUTOLAB potentiostat/galvanostat model PGSTAT 320 power supply unit. The plating solution composition included $[CuCl_2]$ =0.008 M, $[InCl_3]$=0.02 M, $[H_3Cit]$=1.142 M, and [TEA] =0.4 M. The pH of the solution was adjusted with HCl. The CuIn films were subsequently deposited for 1800 s with a constant current. To form a $CuInS_2$ film, CuIn alloys were sulfurized with 5 g of sulfur powder and heated during one-stage and two-stage temperature elevations, respectively. After $CuInS_2$ films were grown, they were electrochemically etched at various voltages. To etch CuS and $Cu_{2-x}S$ phases, the etching system also consisted of two electrodes: Pt for the counter anode electrode and $CuInS_2$ as the working cathode, also with an AUTOLAB potentiostat/galvanostat model PGSTAT 320 power supply unit. The etching solution included K_2SO_4 and KOH. Finally, to analyze the $CuInS_2$ film quality under different treatment conditions, XRD was used to analyze the crystalline structure, SEM was used to examine film morphology, and EDS was used to evaluate film composition.

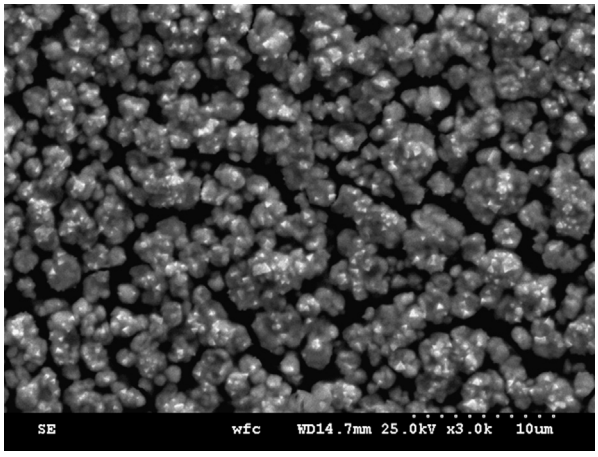


Fig. 1. An SEM image of $CuInS_2$ film sulfurized at 500 °C.

3. Results and discussion

To fabricate $CuInS_2$ films, CuIn precursor films were first electrodeposited and then sulfurized. For sulfurization, a sufficient amount of sulfur powder was added to the CuIn precursor film into a heated tube. If the sulfurization temperature was insufficiently elevated, CuS phases crystals could occur within the film, and CuS phases could become randomly distributed in $CuInS_2$ crystalline structures. Fig. 1 shows an SEM image of a CuIn film sulfurized at 500 °C. The white areas in the image represent crystals of CuS phases, which did not fully react during the sulfurization process. To suppress CuS phases, one-stage and two-stage heat treatments during sulfurization with final temperatures of 500 °C, 550 °C, and 600 °C were conducted. Fig. 2(a) and (b) shows temperature elevation profiles of one-stage [9] and two-stage thermal treatment. For the one-stage thermal treatment, the heating temperature increased from room temperature to final temperatures of 500 °C, 550 °C, and 600 °C. The CuIn film was sulfurized at the final temperature for 130 min. Conversely, Fig. 2(b) presents the temperature elevation for the two-stage heat treatment. The temperature in the tube increased to the first-stage temperature of 150 °C and both the CuIn film and the sulfur powder remained at 150 °C for 10 min. The tube was subsequently heated to final temperatures of 500 °C, 550 °C, and 600 °C, and the Cu–In film was sulfurized at the final temperature for 120 min. SEM was then used to examine the film morphology of the $CuInS_2$ film sulfurized with the one-stage and two-stage heat treatment. Fig. 3(a)–(f) presents the SEM images of the one-stage [9] and two-stage

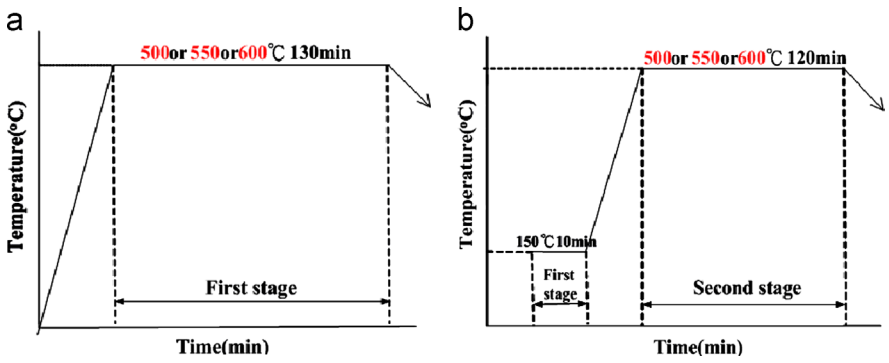


Fig. 2. Temperature elevation profiles for the (a) one-stage and (b) two-stage sulfurized heat treatment.

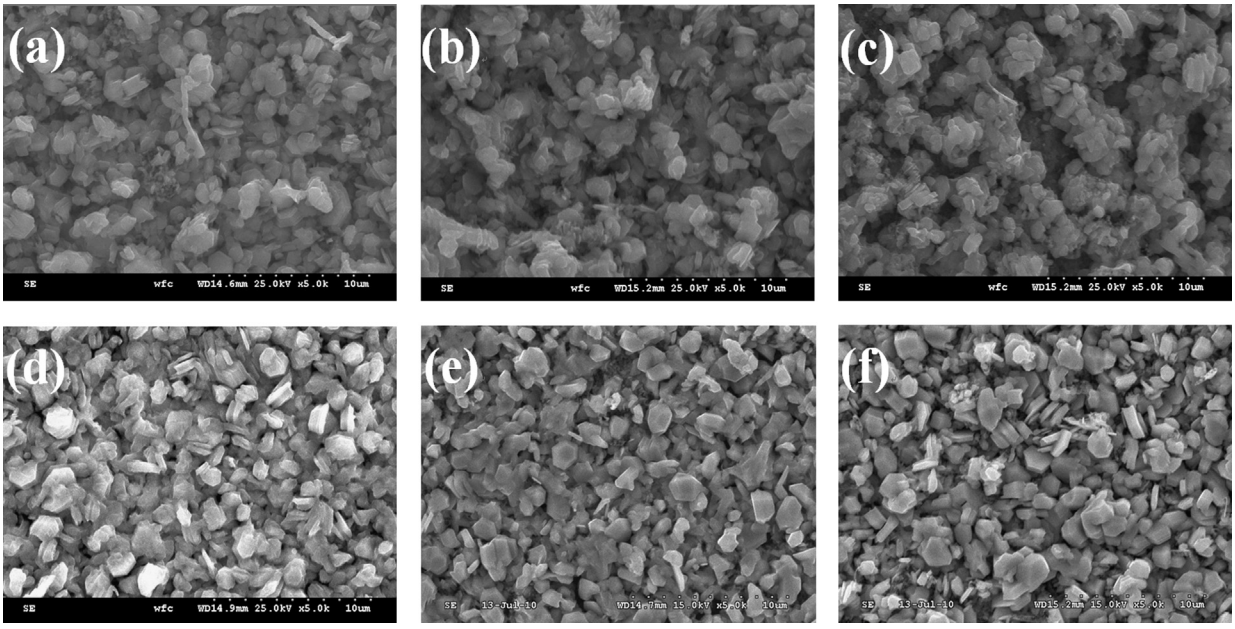


Fig. 3. SEM images of $CuInS_2$ film sulfurized using the one-stage heat treatment with a final temperature of (a) 500 °C, (b) 550 °C, and (c) 600 °C. SEM images of $CuInS_2$ film sulfurized using the two-stage heat treatment with a final temperature of (d) 500 °C, (e) 550 °C, and (f) 600 °C.

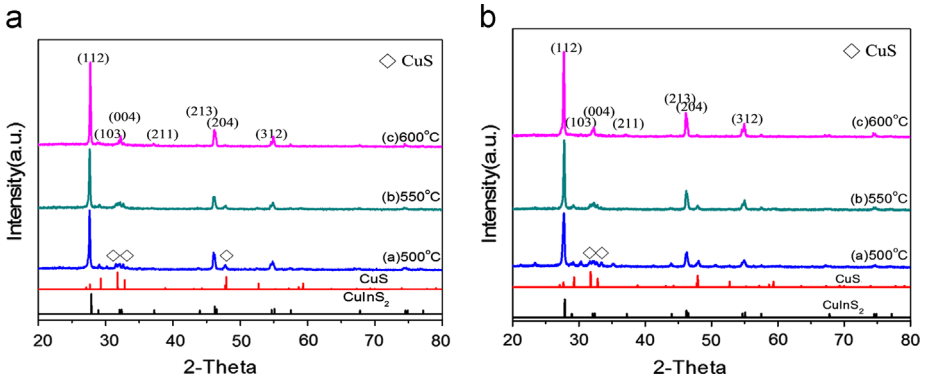


Fig. 4. XRD analyses for $CuInS_2$ sulfurized using (a) the one-stage heat treatment and (b) two-stage heat treatment.

Table 1
Element percentages of the CuInS2 film sulfurized using one-stage and two-stage heat treatment from EDS analyses.

	Cu	In	S	Cu/In	X=S/(Cu+In)
500 °C	**34.26**	**18.98**	**46.76**	**1.8050**	**0.8782**
550 °C	**26.45**	**25.04**	**48.51**	**1.0563**	**0.9421**
600 °C	**25.02**	**24.87**	**50.11**	**1.0060**	**1.0044**
Two-stage heat treatment					
500 °C	**34.73**	**14.47**	**50.80**	**2.4001**	**1.0325**
550 °C	**27.92**	**22.69**	**49.39**	**1.2304**	**0.9758**
600 °C	**26.32**	**26.72**	**46.96**	**0.9850**	**0.8853**
Two-stage heat treatment					

sulfurized films with final temperatures of 500 °C, 550 °C, and 600 °C, respectively. When the final heating temperature was 500 °C, white areas composed of CuS crystal phases were observed both during the one-stage and two-stage heat treatments, as shown in Fig. 3(a) and (d), respectively. When the final temperature was increased to 600 °C, the white areas decreased. Moreover, more compact and larger grain sizes were observed in the $CuInS_2$ film sulfurized with the two-stage heat treatment, as shown by the comparison of the one-stage heat treatment (Fig. 3(c)) versus the two-stage treatment (Fig. 3(f)).

Coinciding with the results of the SEM images, XRD analyses show that $CuInS_2$ underwent a two-stage sulfurization process exhibiting stronger $CuInS_2$ phases. After sulfurization, the main crystalline structure of $CuInS_2$ thin films was a chalcopyrite structure with a preferred orientation in (112). Fig. 4(a) and (b) shows diffraction peaks of the CuS compound at 29.27 °C, 31.78 °C, 32.85 °C, and 47.33 °C. In contrast to form-steady $CuInS_2$ phases, a high concentration of Cu ions and a low-temperature reaction could easily generate CuS from CuIn and S. When the sulfurization temperature increased to 600 °C, the CuS diffraction peaks decreased, causing CuS to transform to the most adequate chemical ratio (1:1:2) of the $CuInS_2$ phases. In addition, the $CuInS_2$ film which underwent a two-stage heat treatment reached higher $CuInS_2$ peaks than the $CuInS_2$ film that underwent a one-stage heat treatment [9]. Moreover, stronger $CuInS_2$ phases were observed as the final temperature increased to 600 °C during both the one-stage and the two-stage heat treatments. The two-stage heating method was more effective than the one-stage heating method because thin films made using the two-stage method were more compact and showed better crystallization. This is because the first stage of heating at 150 °C allowed the sulfur powder to be diffused and uniformly distributed between the CuIn films. During the second stage of heating at the final temperature, the inter-diffused sulfur atoms fully reacted with the CuIn film to form better-crystallized $CuInS_2$ film with fewer impurities. In line with the previous analyses, EDS showed that the CuIn film sulfurized with a two-stage heat treatment at a final temperature of 600 °C was able to form better quality $CuInS_2$ film for solar cell applications. As shown in Table 1, the film treated with a two-stage heat treatment with a final temperature of 600 °C could reach a S/Cu+In ratio approaching 1 compared to films treated under all of the other conditions, indicating that a high-quality $CuInS_2$ film could form.

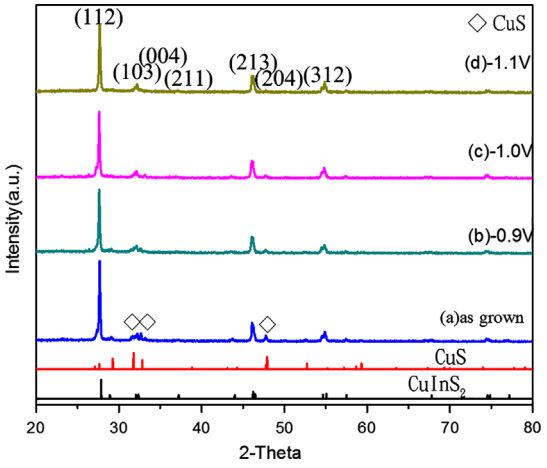


Fig. 5. XRD analyses of the $CuInS_2$ film with and without electrochemical etching.

In addition to the two-stage sulfurized heat treatment, electrochemical etching also provides an alternative method to remove CuS phase crystals. The XRD analyses for the $CuInS_2$ film treated with electrochemical etching are shown in Fig. 5. Before the electrochemical etching process, the CIS thin film was present with CuS phase crystals. Electrochemical etching caused the CuS diffraction peaks to weaken. CuS diffraction peaks at 31.78 °C, 32.85 °C, and 47.33 °C all decreased after etching. While the etching voltage was set at 0.9 V, CuS phases remained. However, when the etching voltage increased from 0.9 to 1.1 V, the undesired CuS phases were completely removed. The SEM images displayed in Fig. 6(a)–(d) shows the same trend. The CuS crystals shown in Fig. 6(a) could be etched using electrochemical etching. Moreover, as the etching voltage increased from 0.9 to 1.1 V, the CuS phases were effectively removed, indicating that electrochemical etching is a useful tool for eliminating

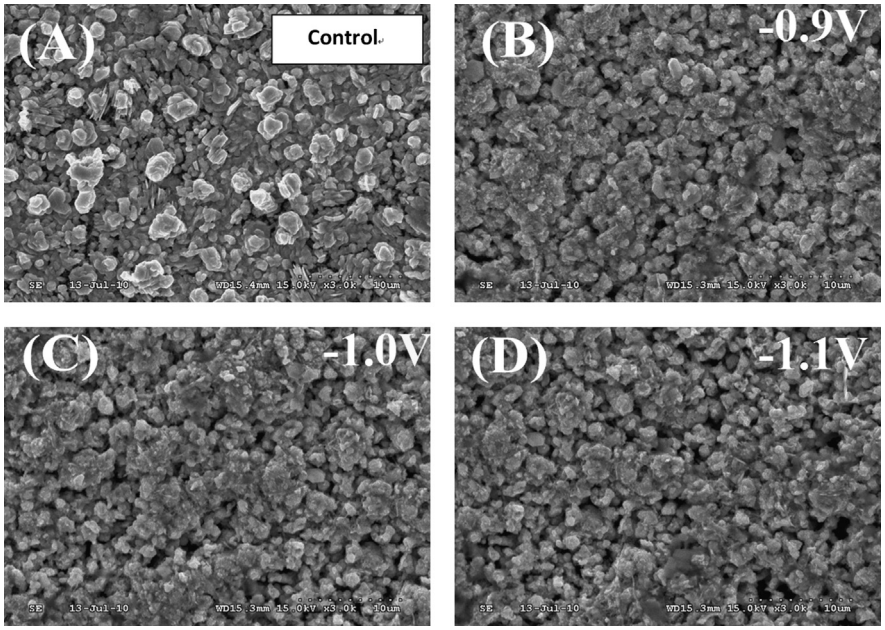
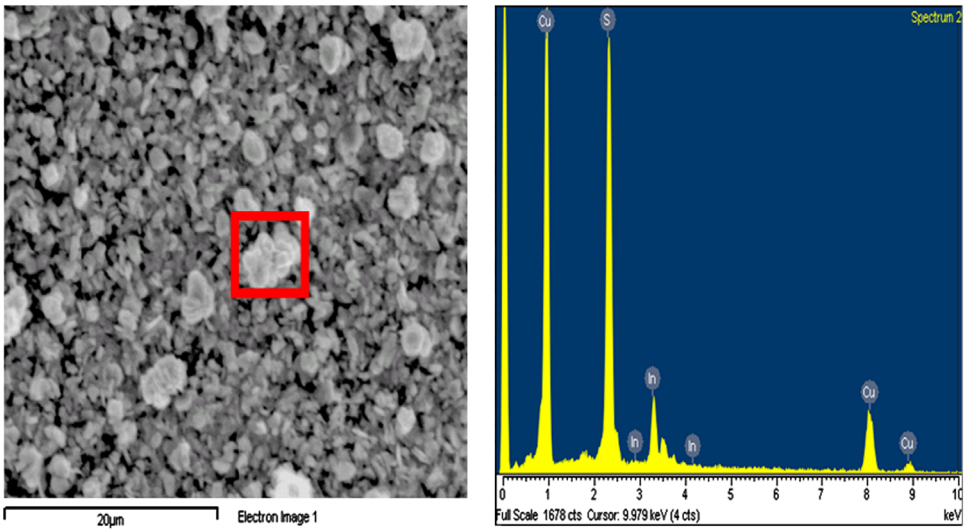


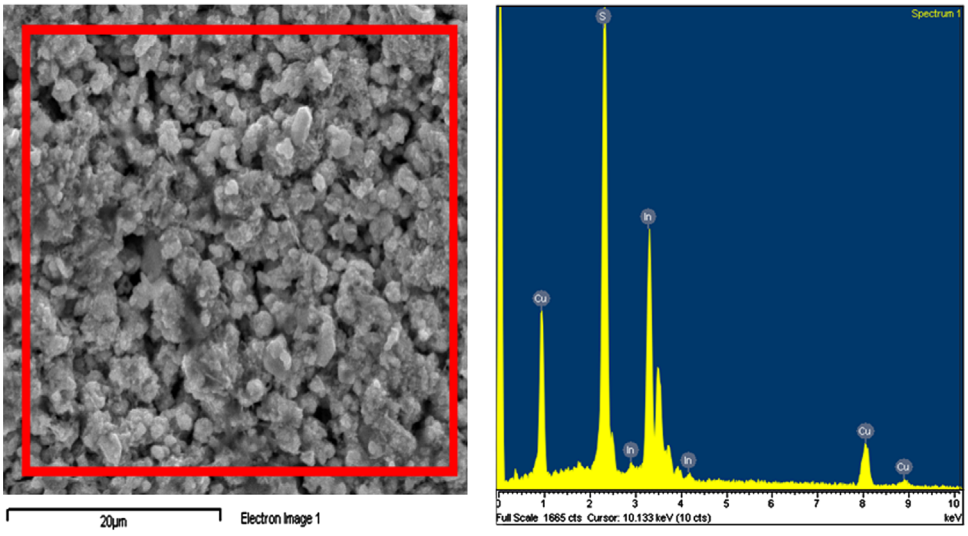
Fig. 6. SEM images of the $CuInS_2$ film (a) without electrochemical etching and (b) electrochemically etched at −0.9 V, (c) −1.0 V, and (d) −1.1 V.

a



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
S K	16.64	1.0020	28.59	0.32	47.07
Cu K	30.09	0.9558	54.19	0.48	45.02
In L	8.76	0.8752	17.22	0.33	7.92
Totals			100.00		

b



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
S K	31.35	1.0705	23.41	0.48	45.66
Cu K	35.85	0.9970	28.74	1.07	28.29
In L	55.87	0.9335	47.84	0.87	26.06
Totals			100.00		

Fig. 7. EDS analyses of the $CuInS_2$ film (a) before electrochemical etching and (b) after electrochemical etching.

CuS phases and for forming high-quality $CuInS_2$ film. Finally, the CuS crystals and the $CuInS_2$ film were examined using EDS analysis. As shown in Fig. 7(a), a 7 μm white grain was analyzed. The CuS phases with an element ratio of Cu/S 1:1 can manifest in the EDS spectrum. After the film was properly etched, the large white grain disappeared, and a preferable ratio of Cu/In/S closer to 1:1:2 was approached, as shown in Fig. 7 (b), indicating that a better quality $CuInS_2$ film could be produced. In addition to the high-temperature thermal treatment that removed CuS from the thin film, electrochemical etching provides an alternative method to remove CuS at low temperatures.

4. Conclusion

Two methods were used in this study to remove undesired CuS phases: a two-stage sulfurized heat treatment and electrochemical etching. Based on XRD, SEM, and EDS analyses, these two methods can effectively eliminate CuS phases to form better quality $CuInS_2$ films. Electrodeposited $CuInS_2$ films with these treatments show promise for future CIS solar cell applications.

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