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Parametric Studies On Corrosion Behaviour of Cu-Zn-Sn Thin Film

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Abstract: In this study, Cu-Zn-Sn (CZT) thin films were deposited on the carbon substrate using the electrodeposition technique. The effect of deposition time on CZT thin film was investigated which was 15 min, 30 min, and 45 min. The structural, morphological, and chemical composition of the prepared thin films were investigated by X-ray diffraction (XRD) analysis, and scanning electron microscopy equipped with energy-dispersive x-ray spectroscopy (SEM-EDX). The prepared films were also examined using Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), and Tafel measurements. It is also can be concluded that deposition times have a strong impact on the appearance and the surface morphology of Cu-Sn-Zn alloy electrodeposits. The Tafel plot revealed that a deposition time of 45 min has the highest corrosion rate means the speed at which metal deteriorates increased. The more positive Ecorr, the higher the corrosion rate while the more negative Ecorr, the lower the corrosion rate.

Keywords: CZT Thin Films, Electrodeposition, Deposition Time

1. Introduction

Electrodeposition process as known as electroplating is a process in which metal ions are deposited onto a conductive surface by passing an electrical current through an electrolytic solution. The conductive surface that receives the metal ions is called the cathode, and the metal to be deposited is called the anode. Electrodeposition is used to deposit various types of coatings, including metals, alloys, and ceramics, onto a variety of substrates such as metals, plastics, and ceramics. These coatings can be used for decorative, functional, or protective purposes[1].

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The thin film is one of the most effective an alternative to silicon photovoltaic technology due to its absorption coefficient being higher than silicon. The ability to manufacture thin film solar cells at high productivity and speed while keeping costs low by using minimal material requirements is the primary motivator[2]. Several thin film materials usually use in photovoltaic cells like amorphous silicon, cadmium telluride (CdTe) and copper indium diselenide (CuInSe2). However, Cd is harmful and the production of CuInSe2 necessitates the release of extremely toxic hydrogen selenide [3]. Therefore, to overcome this problem, copper, zinc, tin and sulphur (CZTS) thin film is an option for photovoltaic application.

CZTS thin films were deposited with several techniques such as spray pyrolysis, sputtering, chemical vapor deposition, physical vapor deposition and electrodeposition[4]. But, electrodeposition is one of the most effective techniques for CZTS grown electrochemically. The fabrication cost is very inexpensive, the deposition process is simple and fully manageable. CZTS has two basic crystalline structures that are similar to stannite and kesterite excluding the different configurations. Kesterite is the Zn-rich wide range, whereas stannite is Zn-poor and the formation of energy of kesterite structure is low. Even so, the CZTS is mostly found as kesterite because it is most stable than the stannite structure[5]

The substrate and copper sheet are immersed in an electrolyte containing metal salts which when dissolved is the source of the positively charged metal cations to be deposited. A potential is then applied to the substrate which acts as the cathode attracting the metal cations toward the substrate. The metal cations are reduced and deposited at the substrate surface[6].

In the present study, a single-step electrochemical growth of Cu-Zn-Sn thin films on carbon-coated substrates with various deposition times is reported. The structural, compositional, morphological, and optical properties were investigated.

2. Experimental Details

All solutions in this work were prepared using analytical grade reagents and deionized water. All experiments were carried out in 100 ml electrolytes prepared with deionized water.

2.1 Preparation of Substrates

The substrate involves in the preparation of Cu-Zn-Sn thin film is carbon with a dimension of 45 mm length, 0.9 mm thickness, and 1.8 mm width. First, the substrate is cleaned with sandpaper. After that, immerse the substrate in the NaOH for 3 minutes at 60º C. Then, the substrate is rinsed with acetone, ethanol, sulfuric acid, and deionized water to remove any oil and contaminations on the surface using a dropper and finally dried in air. The substrate that is already dried is put in a container that contains silica gel.

2.2 Electrodeposition of Cu-Zn-Sn

Electrodeposition process was performed for different deposition times (15 min, 30 min, and 45 min) at room temperature in an electrolyte that contained copper (II) chloride (0.25M), zinc (II) chloride (0.45M), and tin (II) chloride (0.35M). Sodium formate (HCOONa), sodium hypophosphite (NaH_2PO_2), and sorbitol as complexing, reducing, and additive agents respectively, were added into a solution containing metal chloride. Sodium hydroxide (NaOH) was added into the solution to reach the desired pH of 5. The solution was magnetically stirred and heated during preparation to get clear and homogeneous solutions. A copper sheet was used as anode while carbon strips were used as the cathode The electrodeposition process was set up as shown in Figure 1.

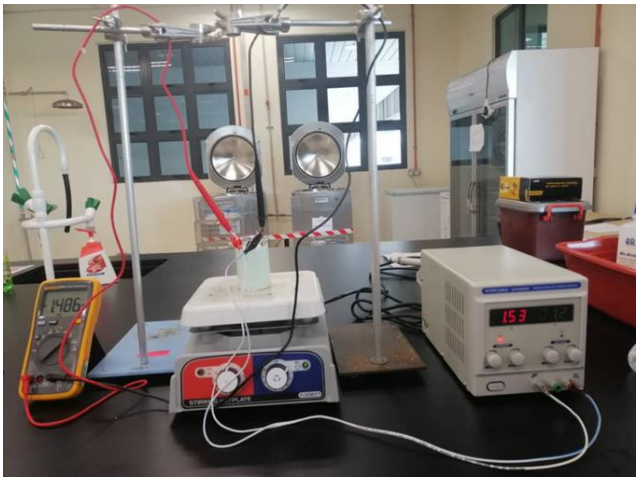


Figure 1: The electrodeposition experiment setup

2.3 Characterization

In this study, structural characterization of the films was carried out by XRD analysis using the PANanalytical X'Pert^3 Powder equipment with CuKα radiation (λ = 1.54060Å) in the 2θ range from 20° to 80°. The surface morphology of the samples was observed by a scanning electron microscope (SEM). The chemical composition of the samples was characterized by an energy-dispersive x-ray spectrometer (EDX).

2.4 Corrosion test

The polarization investigation was performed using Metrohm Autolab Potentiostat/Galvanostat controlled by computer with NOVA 2.0 software, which uses a counter electrode (Pt sheet), reference electrode (Ag/AgCl), and carbon substrate as a working electrode. The polarization curve is known as Tafel plot. The slope is known as anodic and cathodic polarization for the reaction of films. In this curve, the Ecorr and Icorr are referred to as corrosion potential and corrosion current. The following equation derived from Faraday's law was used to calculate the corrosion rate, *r*:

$$C_R = \frac{I_{corr} KEW}{dA} \qquad \text{Eq. 1}$$

where EW is the equivalent weight (g/mol), A is the area of the sample involved, d is density of alloy (g/cm^3) and K is constant, (3272 mm/year) for corrosion rate.

3. Results and Discussion

3.1 X-ray Diffraction analysis

Fig. 2 shows the XRD patterns of Cu-Zn-Sn (CZT) thin films for different deposition times. In this study, the XRD patterns of CZT thin film deposited at deposition times of 15 min, 30 min, and 45 min. As shown in the XRD plot of CZT thin film obtained on the carbon substrate reveal the distinct diffraction peaks obtained at 26.5º, 36.37º, 43.24º, 50.40º, and 74.17º angles corresponding to (112), (200), (220), (312) and (332) planes, according to characteristics of kesterite structure (JCPDS card no: 00-26-0575). There is a dominant and intense peak with a plane of (112) for 15 min but the intensity peak decrease when the deposition time increase. The XRD pattern shows the degradation of the CZT thin film upon deposition at 45 min with the disappearance and decrease of peak intensities; (112) and (312) diffraction peaks become relatively smaller and broader. In the previous research, the intensity

peak increased when the deposition time increased [7]. This result was consistent with what was observed during the 45-minute deposition time because the solution begrimed and turned black.

Therefore, the crystalline quality of films deposited at 45 min is slightly degraded. Furthermore, different CZT structures, such as Cu_5Zn_8 and $Cu_{10}Sn_3$, are likely to exist in films[8].

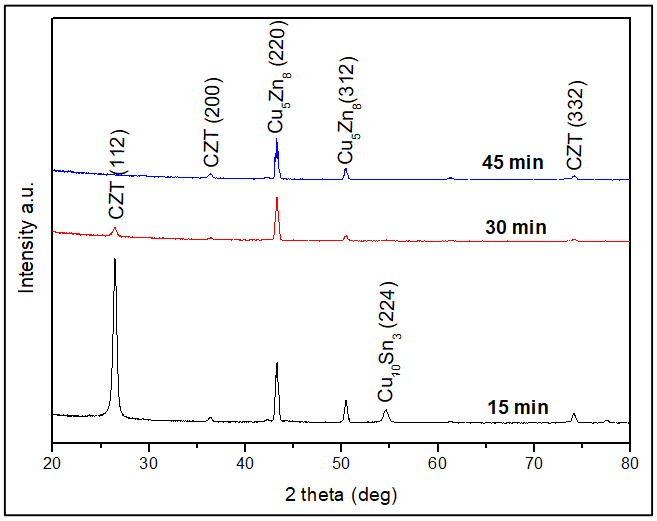
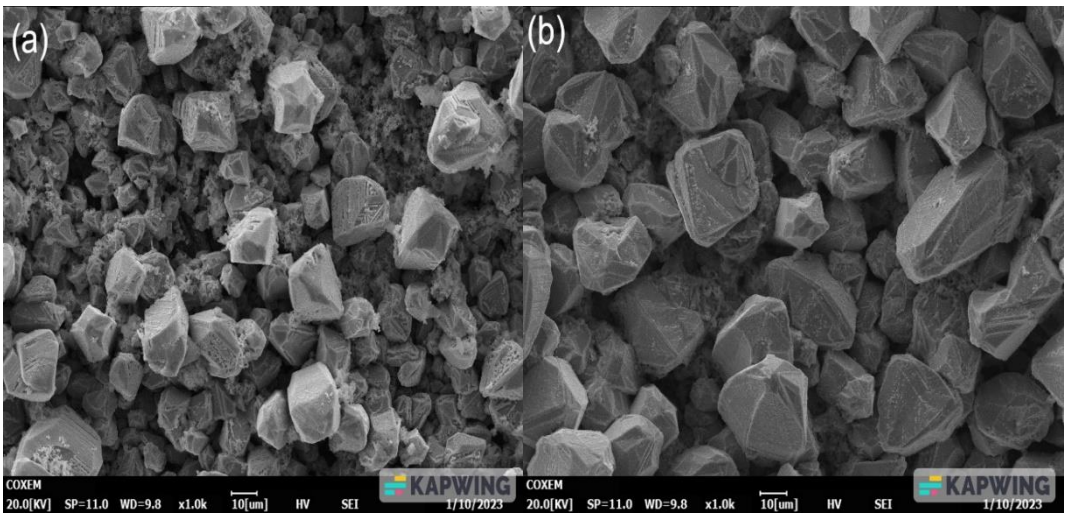


Figure 2: The XRD pattern of CZTS thin film at different deposition times of 15 min, 30 min, and 45 min

3.2 Surface morphology and chemical composition

The Scanning Electron Microscopy (SEM) surface images of CZT films deposited on carbon substrate after the electrodeposition process at different deposition times as shown in Figure 3. In this study, the electroplating process varied at 15 min, 30 min and 45 min. The surface morphology of films changes with the increase of the deposition time. The deposited film on 15 min (Figure 3a) shows less compact and more porous structures in the film. For deposition of 30 min (Figure 3b) shows the structures more apparent grain structures and becomes homogeneous. As the deposition time increases up to 45 min (Figure 3c), the film's surface becomes more compact with large densely packed grains. In short, the surfaces of all the samples are densely packed with well-shaped grains. Other than that, the particle size of samples increases when increasing the deposition time [9]. As a result, we conclude that surface morphology is strongly influenced by deposition time.



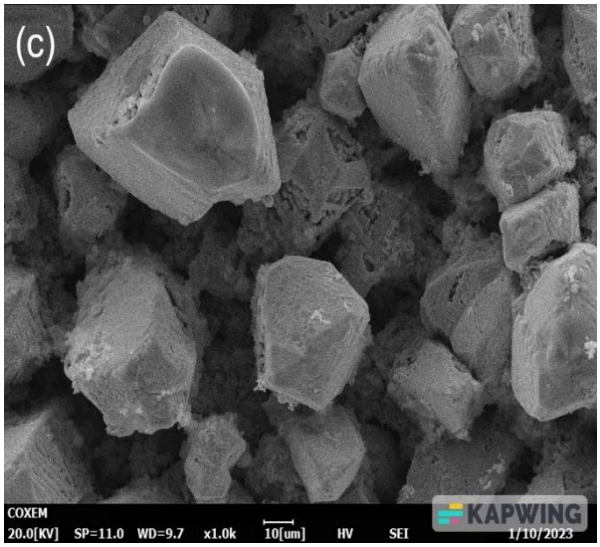
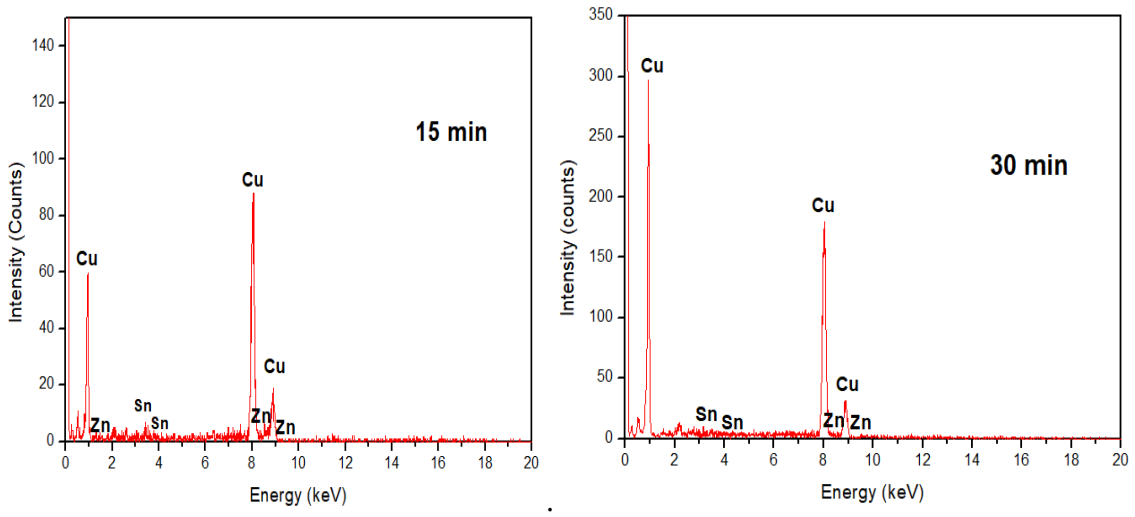


Figure 3: Surface Morphology of the electrodeposited CZT thin films in different deposition times (a) 15 min (b) 30 min (c) 45 min

An energy-dispersed X-ray analysis (EDX) is performed to detect the elemental and quantitative composition of the coating layer at different deposition times. Figure 4 shows the EDX data of Cu-Zn-Sn coated on a carbon substrate with 3A of current. From the figure, it's can conclude that the copper element has the highest composition other than zinc and tin element at different times in Cu-Zn-Sn films. Zinc element has the lowest composition at all deposition times. This could defect that occurs in the electroplating process and the Zn alloy not coated well on a substrate. Thus, the Zn composition is expectedly to increase by increasing the deposition time[10]



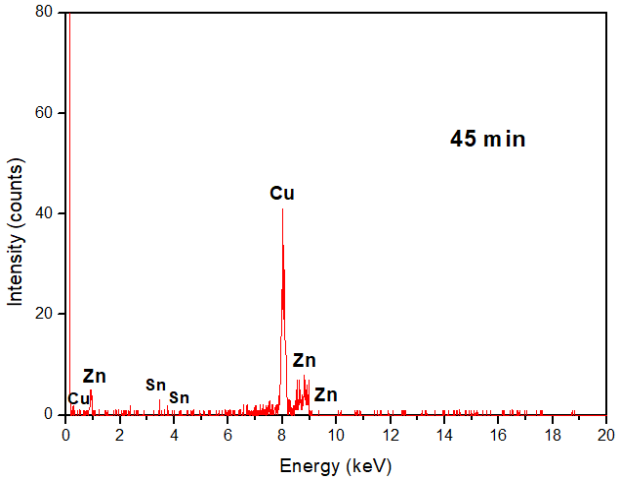


Figure 4: EDX data of Cu-Zn-Sn films for different deposition times

3.3 Electrochemical corrosion behaviour of Cu-Sn-Zn alloys.

Figure 5 shows the Cyclic Voltammetry (CV) plot performed in the range from -0.1V to 0.1 V at a scanning rate of 1 mVs^{-1}. The reduction peaks for Cu^{2+} are between 0.98V to 0.57V, and for Sn^{2+} are between 0.15V to -0.19V while the reduction peaks for Zn^{2+} are between -0.45V to -0.89V. There are two oxidation peaks where between 0.65V to 1.27V: The required potential to deposit the element was mentioned in the previous study [10]

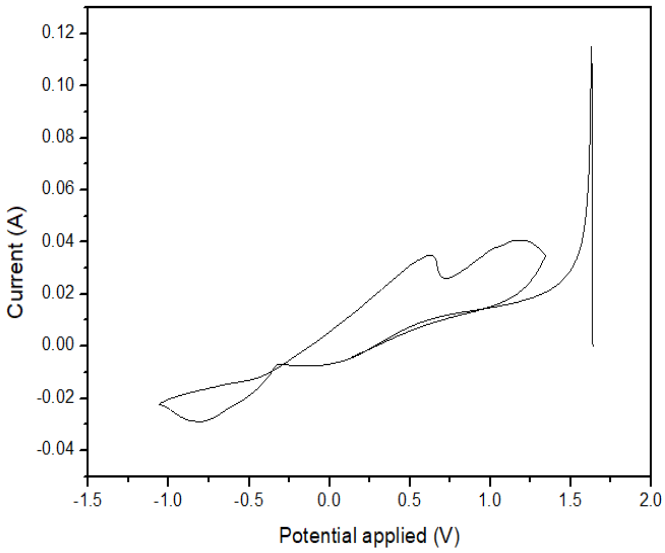


Figure 5: The Cyclic Voltammetry (CV) curve of CZT thin film electrodeposited on a carbon substrate

Figure 6, Figure 7, and Figure 8 show the Tafel plot of CZTS thin film grown electrochemically on the carbon substrate. The specimen area measured 1 cm × 1 cm. The curve shows anodic and cathodic polarization for the reaction of CZTS thin film. The more positive Ecorr, the higher the corrosion rate while the more negative Ecorr, the lower the corrosion rate[11]. Table 1 depicts the corrosion potential, corrosion current, anodic slope, cathodic slope and corrosion rate of CZTS thin film at different deposition times. As depicted in the figures, a deposition time of 45 min has the highest corrosion rate than 15 min and 30 min. Therefore, the sample at 45 min has the highest rate of deterioration.

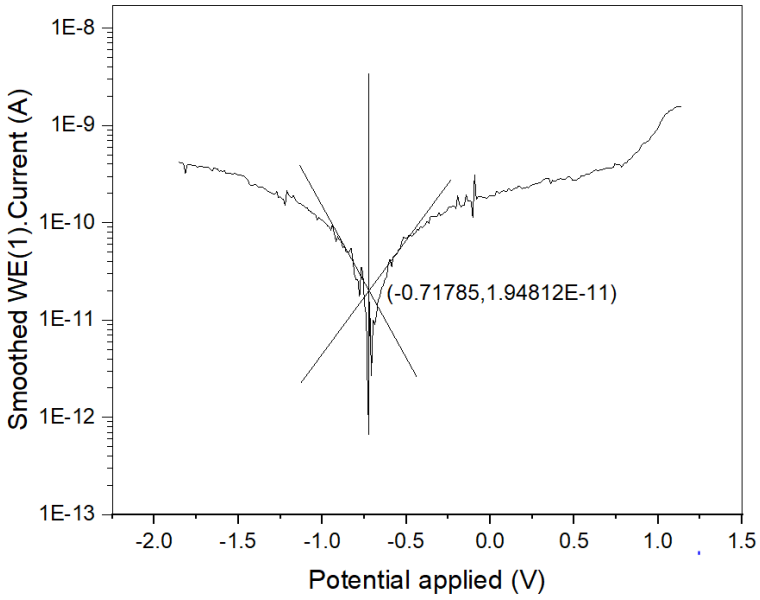


Figure 6: Tafel polarization plot of CZTS thin film for a deposition time of 15 min

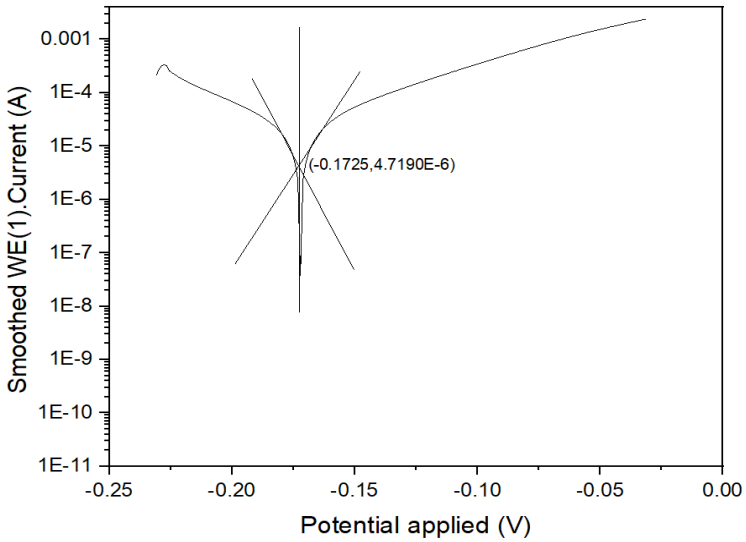


Figure 7: Tafel polarization plot of CZTS thin film for a deposition time of 30 min

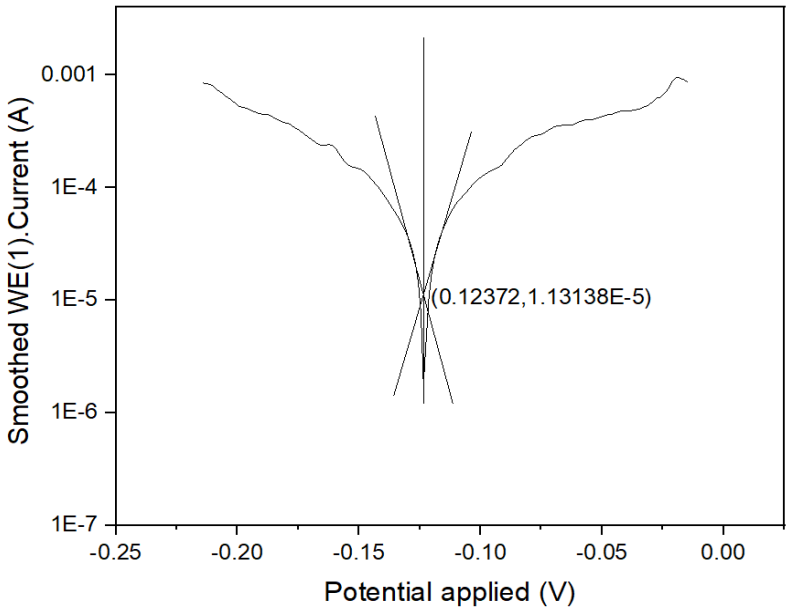


Figure 8: Tafel polarization plot of CZTS thin film for a deposition time of 45 min

Table 1: Electrochemical parameters of CZTS thin film obtained from the Tafel method at different deposition times

Deposition time	E_{corr} (V)	I_{corr} (A)	βa (V/dec)	Bc (V/dec)	Corrosion rate (mm/year)
15 min	-0.71785	1.9481E-11	-3.8754	0.11672	2.0E-7
30 min	-0.1725	4.7190E-6	0.02780	0.02862	0.04845
45 min	0.12372	1.1314E-5	0.01666	0.01569	0.11619

4. Conclusion

In summary, we have reported the deposition time effect on CZT thin films obtained by electrochemical deposition. All the films showed distinct diffraction peaks of the single pure phase of the kesterite structure. The SEM images showed that the obtained films become more homogeneous and compact by increasing the deposition times. EDX analysis revealed that the copper element has the highest percentage composition in films. The Tafel plot revealed that a deposition time of 45 min has the highest corrosion rate means the speed at which metal deteriorates an increase.

Acknowledgment

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