

FABRICATION OF CIGS FILMS BY ONE-STEP PULSE ELECTRODEPOSITION ON Mo/SLG SUBSTRATES

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In this study, we used low-cost non-vacuum electrochemical coating methods to prepare Cu (In_{1-x}Ga_x) Se₂ precursor films on Mo/SLG substrates for the CIGS absorber applications. To find the most suitable growth conditions, we applied two types of electrodeposition conditions: the constant potential electrodeposition and pulsed electrodeposition. To examine the material properties of the film, the surface morphology, composition, and crystal structure analyses of the CIGS films were investigated by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD), respectively. The results show that pulse electrodeposition process with an appropriate duty cycle, pulse period and deposition voltage could significantly improve the CIGS film quality. The pulse deposited CIGS films show promises for future CIGS solar cell applications.

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Keyword: Pulse; Duty cycle; One-step electrodeposition; Cu(In,Ga)Se₂; Thin film solar cell

1. Introduction

With technology booming, oil, coal charcoal, natural gas, and fossil fuels are the main energy sources today. However, the shortage and the pollution caused by these energy sources have raised public awareness of the need of alternative energy sources. Among all the alternative energy, the solar energy is currently one of the most potential green energy power because it is inexhaustible energy, running without fuel, and generating low pollution. Since the first photovoltaic semiconductor device was invented at Bell Labs in 1954 [1], various materials including Si [2], GaAs [3], and chalcogenide materials [4] have been utilized to fabricate photovoltaic devices. Among these photovoltaic materials, chalcogenide materials have attracted growing attention since a p-type crystalline CuInSe₂ was utilized to fabricate photodetectors in 1974 [5]. Recently, Cu (In_{1-x}Ga_x) Se₂ have been intensively studied because the CIGS-based solar cell can achieve a high solar power conversion efficiency [6]. To fabricate CIGS solar cells, CIGS absorber films are crucial to the overall performance of the solar cells. Until now, various techniques including sputtering, co-evaporation, selenization, and electrodeposition have been reported [7-10]. Electrochemical deposition as one of the non-vacuum methods to grow the CIGS

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absorber films has the advantages of simple process, low cost, and large area production [11, 12]. However, the material quality of the CIGS film prepared by electro-deposition methods is still inferior to that of the film grown in vacuum methods. Therefore, developments of the electrochemical techniques have been conducted by some research groups. Especially, the pulse electrodeposition has been demonstrated by Liu et al.[13] and Jadhav et al. [14] because the pulse electrodeposition can enhance the film quality and mitigate the impurities. In this research, we used one-step pulse electrodeposition to grow the CIGS precursor films. In addition, pulsed deposition parameters such as the duty cycle, pulse period and deposition voltage density have been adjusted to find the optimal growth condition. To evaluate the film quality, multiple material analyses including scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were performed. The results indicate that pulse electrodeposition process with an appropriate duty cycle, pulse frequency and deposition current density could significantly improve the CIGS film quality.

2. Experimental

In this study, we deposited the CIGS precursor layer on top of the Mo/ Soda lime glass (SLG) substrates. We first cleaned the substrates with an alkaline detergent, followed by sequential isopropyl alcohol, acetone, alcohol, and DI Water. The CIGS films were grown on Mo/SLG glass substrates by the co-deposition (electro-deposition) method. The three-electrode electro-deposition system consisted of the reference electrode of silver / silver chloride (Ag / AgCl), the counter electrode of platinum wire (Pt), and the working electrode of Mo/ SLG glasses. AUTOLAB PGSTAT320 Potentiostat Galvanostat was used to control the potential profile during the deposition. The electro-deposition solution compositions and the deposition conditions are shown in Table 1. After deposition, the CIGS films were annealed in a quartz tube furnace under vacuum condition. This annealing time can be divided into two stages. In the first stage, the temperature increased from 20 °C to 550 °C for 55 min. Then, in the second stage, the temperature remained at 550 °C for 1 hour, shown in Figure 1. The annealing temperature profile is shown in Fig. 1. To evaluate the film quality, XRD was used to analyze the crystalline structure. To study the surface morphology, SEM was used to monitor the surface. Furthermore, the composition of Cu, In, Ga, and Se of CIGS thin films were analyzed by EDS.

Table 1. Pulse electrodeposition solution composition and deposition conditions.

Cu(In _{1-x} , Ga _x)Se ₂ Plating Solution	
CuCl ₂	3mM
InCl ₃	45mM
GaCl ₃	65mM
H ₂ SeO ₃	15mM
C ₆ H ₅ Na ₃ O ₇	50mM
pH	1.7
I(ASD)	0.1 ~ 0.5
Deposition time	30~120min

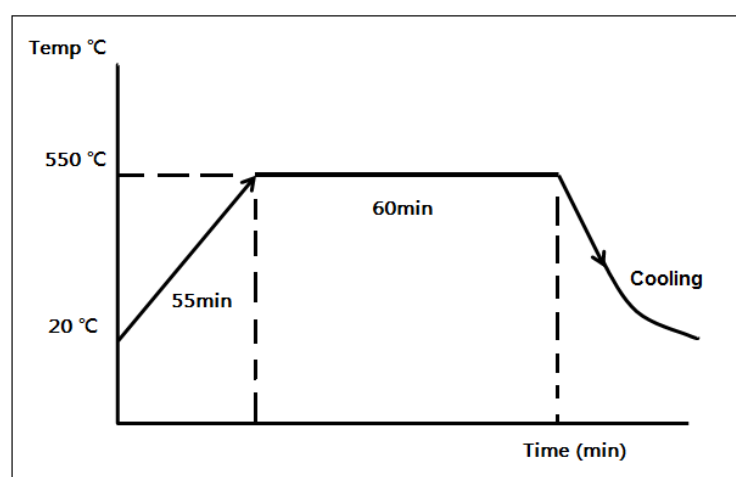


Fig. 1 The temperature profile of the two-stage annealing .

3. Results and discussion

The main purpose of this study is to find the most suitable CIGS precursor film deposition potential. In the beginning, to find the suitable the deposition potential, the deposition voltages of -1.5 V, -1.6 V, -1.8 V, -2.0 V, and -2.2 V were applied to grow the CIGS precursor film while the pH of the electrolyte solution was adjusted to 1.6 with the addition of ammonia (NH₄OH) or hydrochloric acid (HCl). Moreover, the deposition time was 60 min. To investigate the deposition conditions, SEM images of the films grown in various voltages are shown in Fig. 2 (a)-(e). The results reveal that dense and uniform films could be deposited at the deposition voltages below -1.8 V. As the deposition voltage increased to -2.0 V, and 2.2 V, the adhesion of the coating surface became worse, and the film became rougher. The films began to peel off. Moreover, EDS analysis is shown in Table 2. Since of greater than 1 is p-type, less than 1 is n-type, we might choose the deposition voltage of -1.8V to obtain a p-type CIGS absorber film.

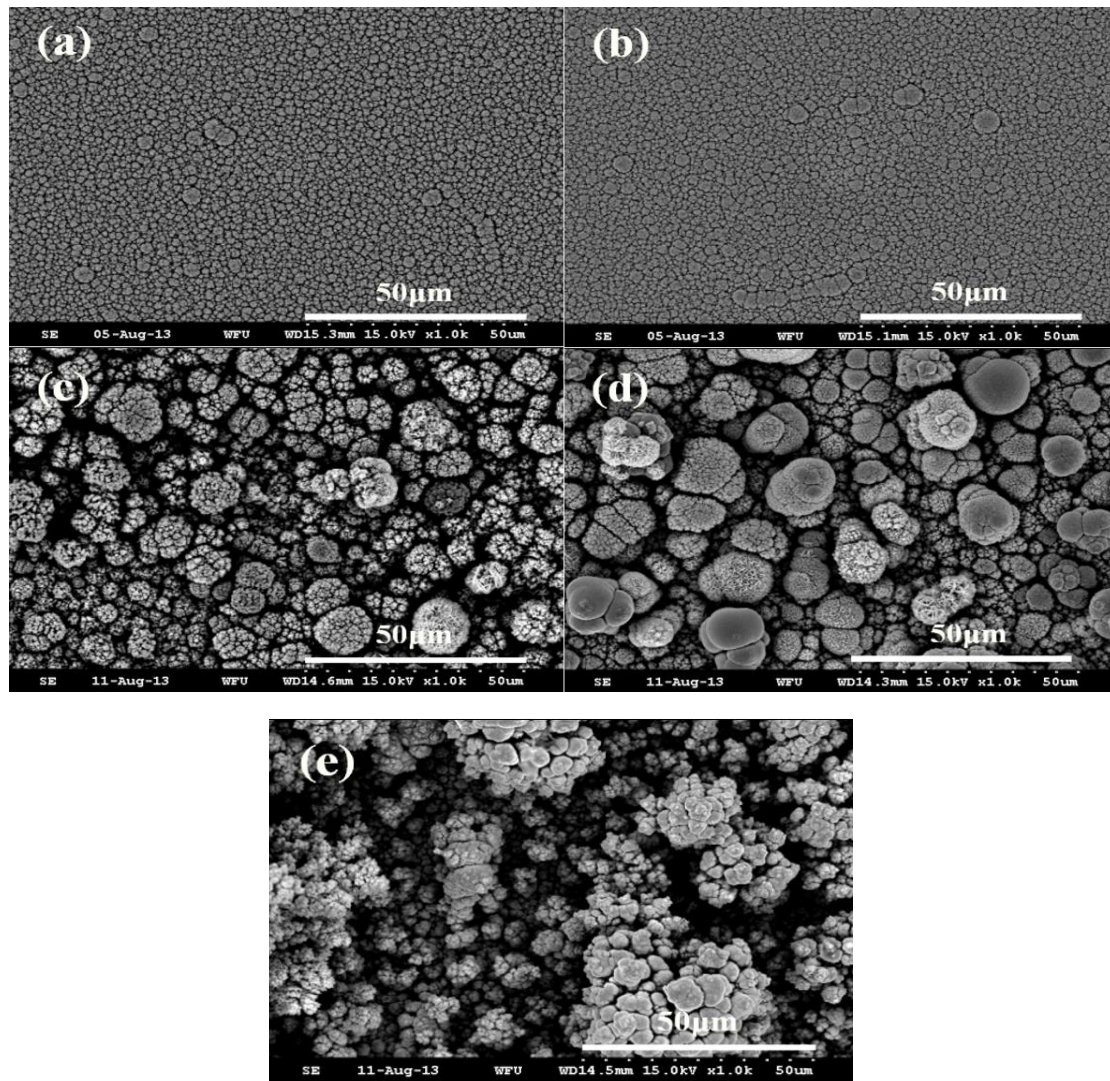


Fig.2 SEM images of the deposited film grown at voltages of (a) -1.5V (b) -1.6V (c) -1.8V (d) -2.0V (e) -2. 2V

Table 2 EDS analysis of the compositions of the film grown at various voltages

	Cu	In	Ga	Se	Atomic %	Cu/(In+Ga)
-1.5V	18.67	12.18	0	69.15	100	1.5328
-1.6V	17.58	17.81	0	46.61	100	0.9870
-1.8V	24.53	9.51	0.17	65.78	100	2.5340
-2.0V	22.12	10.72	1.19	65.97	100	1.8570
-2.2V	15.92	36.30	0.94	46.84	100	0.4274

To further improve the film quality, we used the pulse deposition instead of the constant voltage or constant voltage deposition. The pulse voltage deposition profile is shown in Fig. 3. T_{on} is the time when the deposition voltage is applied and T_{off} is the time when no voltage is applied. As for the pulse deposition, we could vary the deposition period and the deposition duty cycle. The pulse period is $T_{on}+T_{off}$. The deposition duty cycle is defined as Eq. 1. To evaluate the pulse-deposited film quality, SEM and XRD was used to analyze the deposited films.

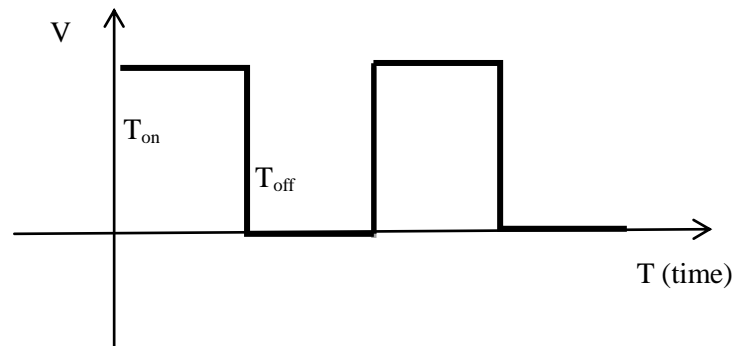


Fig. 3. The pulse voltage deposition profile

$$\text{The deposition duty cycle} = \frac{T_{on}}{T_{on}+T_{off}} \quad (1)$$

To investigate the impact of the deposition duty cycle, we first set the deposition period to be 0.5 and vary the duty cycle. SEM images of the deposited film with duty cycles from 0.2 to 1 are shown in Fig. 4 (a)- (f). The results reveal that the duty cycle had to be larger than 0.5 to deposit the CIGS film and a uniform and compact film could be deposited at the deposition duty cycle of 0.5. Consistent with the SEM images, XRD patterns as shown in Fig. 5 also shows that the annealed films with the duty cycle greater than 0.5 could exhibit strong crystallization phases. However, the crystallization did not vary a lot.

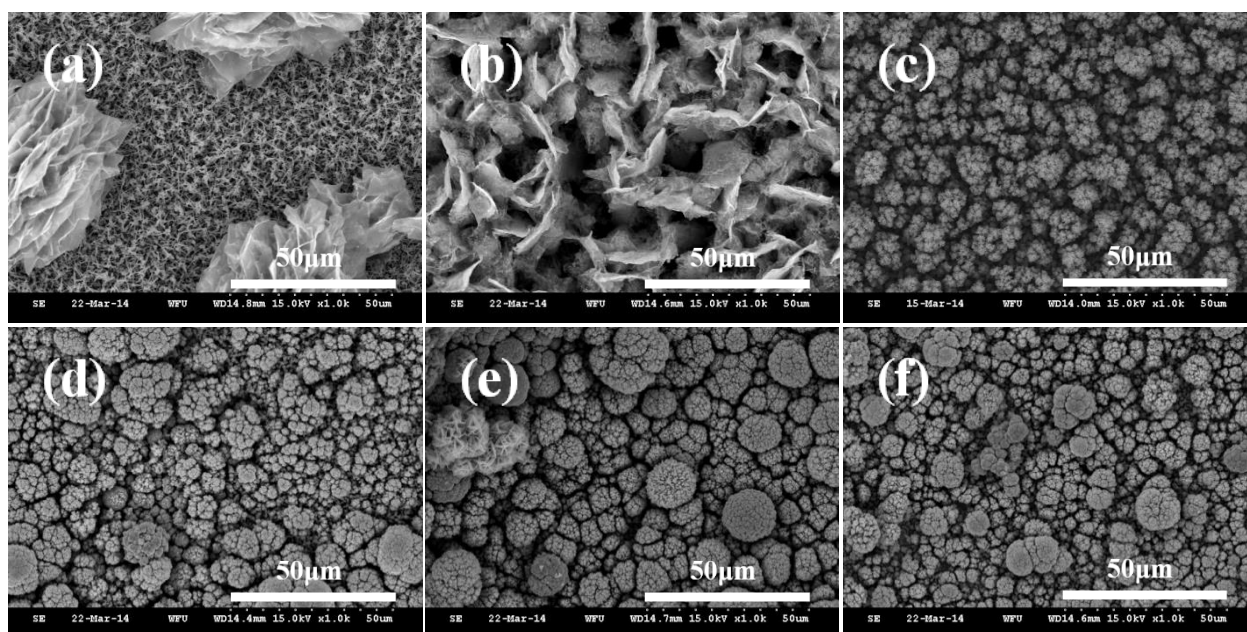


Fig. 4 SEM images of the deposited film with duty cycles of (a) 0.2 (b) 0.4 (c) 0.5 (d) 0.6 (e) 0.8 (f) 1

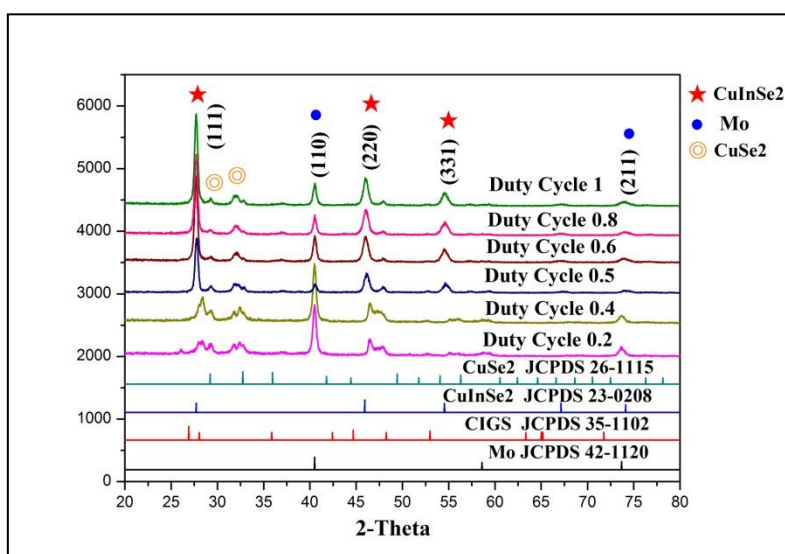


Fig. 5 XRD patterns of the annealed film with various duty cycles microstructure

Moreover, to examine the influence of the deposition period, we set the duty cycle to be 0.5 and varied the deposition periods from 10 to 0.01 seconds ($T_{on} = 5$ to 0.005 seconds). SEM images of the deposited films with various deposition periods before and after annealing are shown in Fig. 7. Based on the SEM images, the most dense and compact film could be deposited with the deposition period of 0.01 seconds.

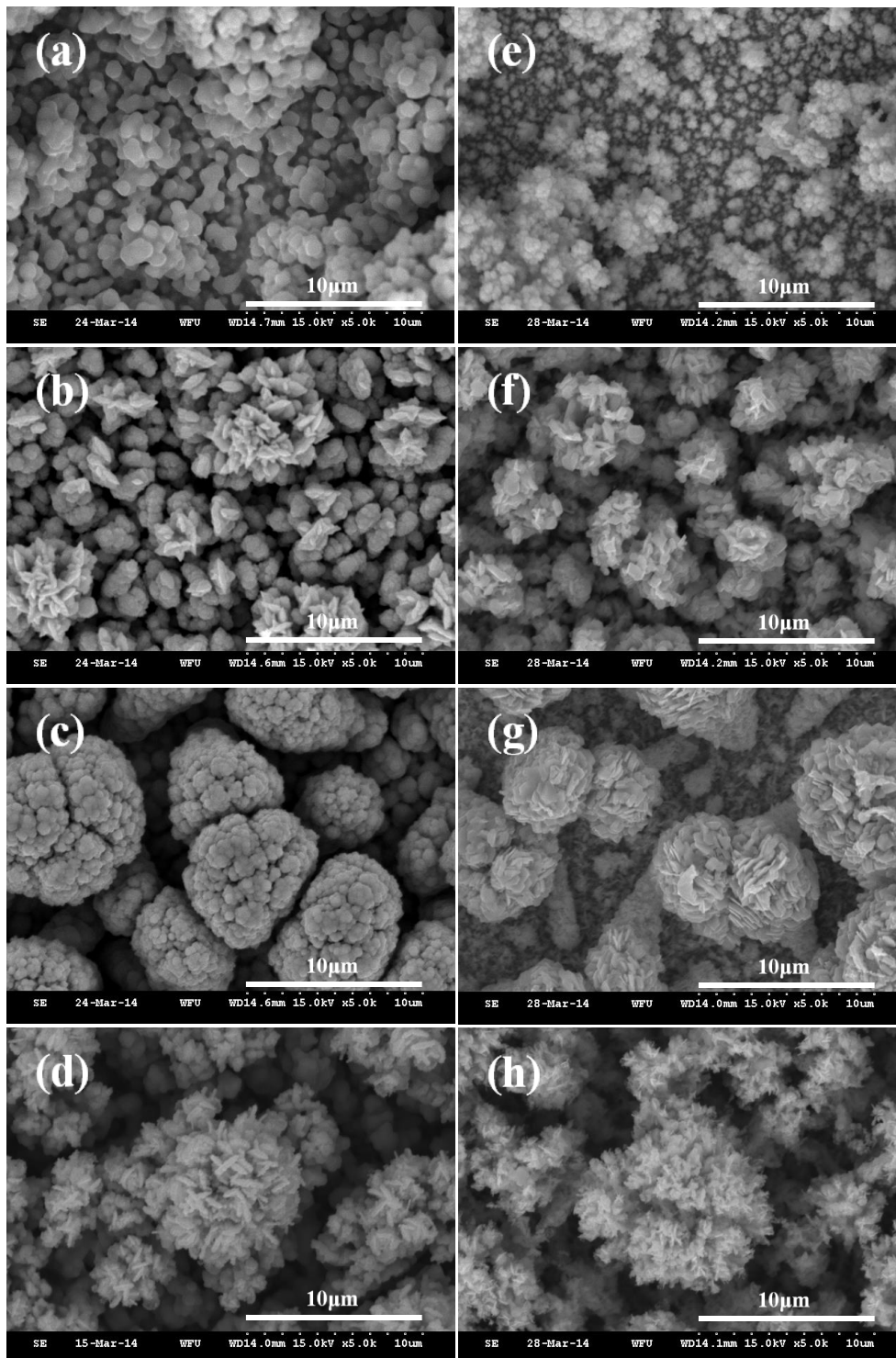


Fig. 7 SEM images of the surface morphology of the as-deposition deposited film with the deposition period of (a) 10 (b) 1 (c) 0.1 (d) 0.01 seconds. SEM images of the annealed film with the deposition period of (e) 10 (f) 1 (g) 0.1 (h) 0.01 seconds.

Consistent with the SEM images, the strongest crystalline phases could be found on the deposited film with the deposition period of 0.01 second ($T_{on} = 0.005$ second, duty cycle = 0.5) as shown in the XRD patterns of Fig. 8.

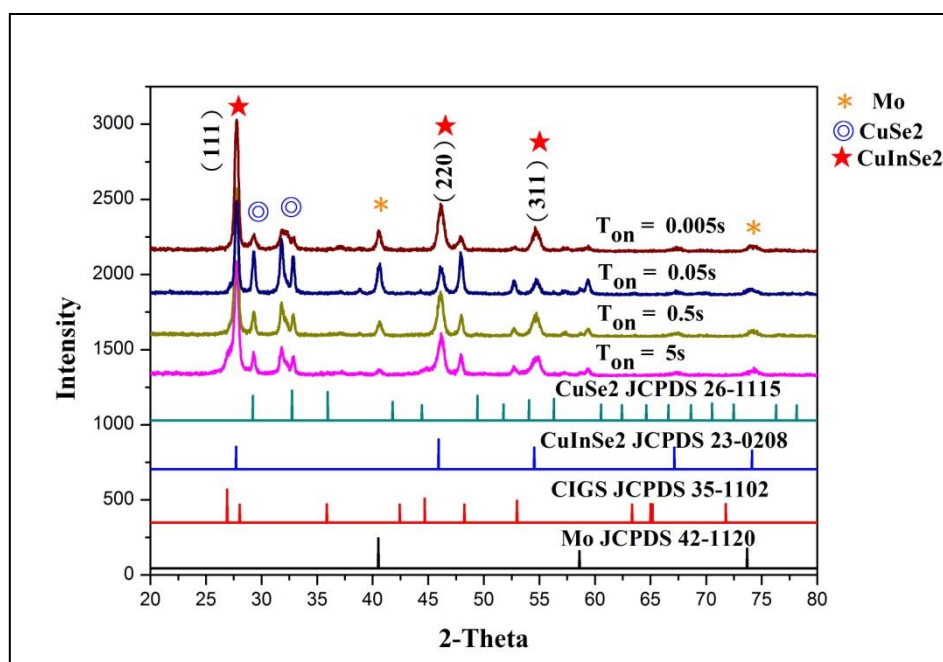


Fig. 8. XRD patterns of the annealed film with various deposition T_{on} .
(The deposition period = $2 \times T_{on}$ and the duty cycle = 0.5)

4. Conclusion

In this research, CIGS films were deposited on Mo/SLG substrates with pulse deposition methods. Multiple material analyses including SEM, XRD, and EDS were utilized to examine the deposition parameters. The results indicate that the pulse deposition parameters including the pulse deposition voltage, the pulse deposition period, and the duty cycle could influence the film quality of the deposited CIGS film.

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