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Materials

Synthesis of the $CuInSe_2$ thin film for solar cells using the electrodeposition technique and Taguchi method

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Abstract: The Taguchi method was used to obtain the optimum electrodeposition parameters for the synthesis of the $CuInSe_2$ thin film for solar cells. The parameters consist of annealing temperature, current density, $CuCl_2$ concentration, $FeCl_3$ concentration, H_2SeO_3 concentration, TEA amount, pH value, and deposition time. The experiments were carried out according to an $L_{18}(2^1 3^7)$ table. An X-ray diffractometer (XRD) and a scanning electron microscope (SEM) were respectively used to analyze the phases and observe the microstructure and the grain size of the $CuInSe_2$ film before and after annealing treatment. The results showed that the $CuInSe_2$ phase was deposited with a preferred plane (112) parallel to the substrate surface. The optimum parameters are as follows: current density, 7 mA/cm^2; $CuCl_2$ concentration, 10 mM; $FeCl_3$ concentration, 50 mM; H_2SeO_3 concentration, 15 mM; TEA amount, 0 mL; pH value, 1.65; deposition time, 10 min; and annealing temperature, 500°C.

Key words: $CuInSe_2$ (CIS); thin film solar cell; electrodeposition; Taguchi method

1. Introduction

Owing to the crisis of petroleum shortage, other energy sources are urgently being searched and deeply researched for replacing petroleum. Among these energy sources, the thin film solar cell is a promising candidate. There are some materials, *e.g.* CdTe, CdSe, ZnP_2, Zn_3P_2, $CuInSe_2$, and $CuInGaSe_2$, which have a direct energy gap and then have a relatively large optical absorption coefficient. They can be used as active materials for thin film solar cells. The films can be prepared by various methods, *e.g.* spray pyrolysis [1-2], molecular beam epitaxy (MBE) [3], vacuum evaporation [4-5], sublimation [6], chemical bath deposition, and electrodeposition [7-8].

The $CuInSe_2$ thin film, whose band gap is about 1 eV and absorption coefficient is larger than 10^{-5} cm^{-1}, is one of the best absorber materials for use in solar cells. It can be prepared by electrodeposition technique, which has some advantages, *e.g.* low cost, low operation temperature, easy operation, and large deposited area. There are several reports concerning the preparation of $CuInSe_2$ thin films by electrodeposition [9-14]. However, there are several factors such as electrical current density, composition and operation condition of plating bath, and annealing condition, which can affect the properties of $CuInSe_2$ thin films. Therefore, it is quite difficult to determine the optimal parameters of electrodeposition for the $CuInSe_2$ thin film with good quality.

Between 1950 and 1960, Taguchi developed a method for robust design [15]. He believed that the loss of product quality results in an ultimate cost to society and then developed a quality loss function of the deviation of quality from its target value. He also defined the signal-to-noise ratio (S/N) for the response analysis of selected physical quantities. The loss function or the signal-to-noise ratio can be used to determine the product quality or to compare the product performance. The signal-to-noise ratio can be combined with the orthogonal array for the design of experiments to improve the product and process.

The Taguchi method is very suitable for the study of thin film coatings, because the properties of thin film coatings are affected by several deposition parameters that can be optimized by the Taguchi method with less labor, time, cost, and better quality. The Taguchi method has been applied to various thin film coatings, such as copper deposition on printed circuit

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boards [16], nickel-coated protein chips by electroplating technology [17], TiN coatings on cutting tools by cathodic arc physical vapor deposition [18], tungsten coatings deposited by plasma spraying [19], multiple-criteria problems of the VLSI manufacturing process [20], nickel chrome sputtered to A_2O_3 [21], *etc*.

In the present study, the preparation of the $CuInSe_2$ thin film by electrodeposition was further studied by the Taguchi method to determine the optimum electrodeposition parameters for a better quality of the $CuInSe_2$ thin film for solar cells.

2. Experimental detail

A silicon wafer with (001) surface was used as the substrate, on which there was a thin film of native oxide layer. After the standard cleaning procedure, a Mo film about 1 μm thick was deposited on the substrate surface in a sputtering deposition chamber at a back pressure below 2×10^{-6} torr. After dipping in an acetone solution with ultrasonic vibration for 10 min, the $Mo/SiO_2/Si$ structure was then deposited with a film of $CuInSe_2$ about 1 μm thick by the electrodeposition technique. The electrodeposition bath consisted of $CuCl_2$, $InCl_3$, H_2SeO_3, and Triethanolamine (TEA), whose pH value was adjusted by both dilute HCl and NaOH solutions. In the electrodeposition process, a Pt metal plate was used as the anode and the plating bath was not stirred. After rinsing with deionized water, the sample of $CuInSe_2/Mo/SiO_2/Si$ was annealed in vacuum for 30 min at 400 and 500°C.

The sample of $CuInSe_2/Mo/SiO_2/Si$ was characterized before and after annealing. A scanning electron microscope (SEM) (JEOL Ltd JSM-T300A) operated at 20 kV was used to observe the morphology and microstructure. An X-ray diffractometer (XRD) (M03XHF[22]) was used to analyze the crystal structure and to determine the relative amount of $CuInSe_2$ phase in various samples. The chemical composition of the sample was determined by energy dispersive X-ray spectroscope (EDS) equipped in SEM and induced coupling plasma (ICP).

In the Taguchi method, eight factors were taken as variables for controlling the $CuInSe_2$ synthesis for optimizing the electrodeposition of the $CuInSe_2$ film, which are annealing temperature (factor A), current density (factor B), $CuCl_2$ concentration (factor C), $InCl_3$ concentration (factor D), H_2SeO_3 concentration (factor E), TEA amount (factor F), the pH value of plating bath (factor G), and deposition time (factor H). Except that factor A has two levels, the other factors have three levels to be varied for study. These factors and their levels are shown in Table 1. An orthogonal array of $L_{18}(2^1\times3^7)$ shown in Table 2 was selected for study in the Taguchi method. It can be seen that there are in total 18 experiments needed for this study. Among these control factors, factor F (TEA) was added for controlling the reduction reaction of Cu^{2+} ions into Cu metal atoms.

Table 1. Control factors and levels for the electrodeposition of the $CuInSe_2$ thin film

Level	A, Annealing temperature / °C	B, Current density / (mA·cm^{-2})	C, $CuCl_2$ / mM	D, $InCl_3$ / mM	E, H_2SeO_3 / mM	F, TEA / mL	G, pH	H, Deposition time / min
1	400	5	5	25	15	0	1.80	10
2	500	7	10	50	25	2.5	1.65	15
3	—	9	15	75	50	5	1.50	20

In the present study, the integrated intensity of the (112) X-ray diffraction peak from $CuInSe_2$ phase was selected as the object function for the Taguchi method. Since the (112) peak is the most intensive in the X-ray diffraction pattern of $CuInSe_2$, it can be used as the indication for the quality of the $CuInSe_2$ film. In the Taguchi method, the analyses consist of analysis of mean (ANOM) and analysis of variance (ANOVA). From ANOM, the effect of each control factor at a given level on the $CuInSe_2$ film quality can be estimated and then the optimum levels of control factors for the synthesis of the $CuInSe_2$ film with better quality can be obtained. The aim of ANOVA is to estimate the variance in film quality owing to the control factor or the experimental error and to determine the contribution percentage of each control factor.

3. Results and discussion

There are 18 experiments totally in this study; only the results of the 17th and the 18th experiments were selected for description and discussion in detail owing to the medium quality of the 17th experiment sample and the high quality of the 18th experiment sample. Figs. 1(a) and 1(b) depict the SEM views of the $CuInSe_2$ film of the 17th experiment, Fig. 1(b) is the magnification of Fig. 1(a). The film seems compact and consists of essentially spherical particles with a size roughly ranging from 1 to 10 μm. These particles further contain several sub-microsized particles. The EDS pattern of this film is shown in Fig. 2, which reveals that the film contains only Cu, In, and Se. The atomic ratio of Cu, In, and Se is 1:0.57:2.10, which is confirmed by ICP. Fig. 3 depicts the XRD patterns of this film before and after annealing in vacuum at 500°C for 30 min. The $CuInSe_2$ phase is clearly revealed. The background noise of the XRD pattern for the sample after annealing is smaller than that before annealing. This indicates that the annealing treatment can decrease the defects and increase the crystallinity of the film.

Table 2. Orthogonal array of $L_{18}(2^1\times3^7)$ for the experiments

No.	A	B	C	D	E	F	G	H
1	400	5	5	25	15	0	1.8	10
2	400	5	10	50	25	2.5	1.65	15
3	400	5	15	75	50	5	1.5	20
4	400	7	5	25	25	2.5	1.5	20
5	400	7	10	50	50	5	1.8	10
6	400	7	15	75	15	0	1.65	15
7	400	9	5	50	15	5	1.65	20
8	400	9	10	75	25	0	1.5	10
9	400	9	15	25	50	2.5	1.8	15
10	500	5	5	75	50	2.5	1.65	10
11	500	5	10	25	15	5	1.5	15
12	500	5	15	50	25	0	1.8	20
13	500	7	5	50	50	0	1.5	15
14	500	7	10	75	15	2.5	1.8	20
15	500	7	15	25	25	5	1.65	10
16	500	9	5	75	25	5	1.8	15
17	500	9	10	25	50	0	1.65	20
18	500	9	15	50	15	2.5	1.5	10

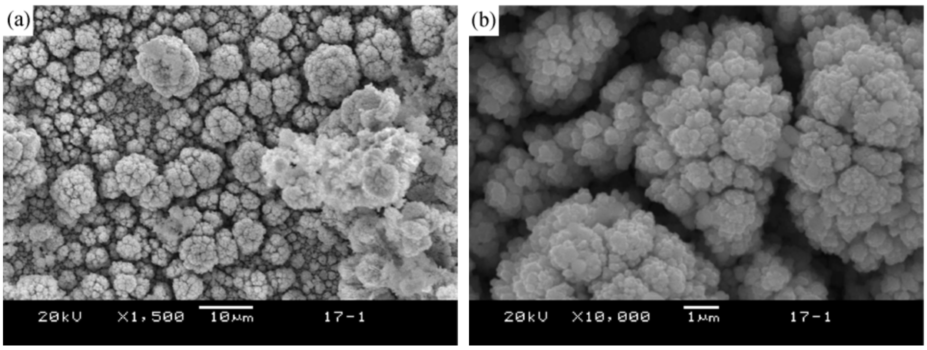

Fig. 1 SEM views of the $CuInSe_2$ film of the 17th experiment, (b) is the magnification of (a).

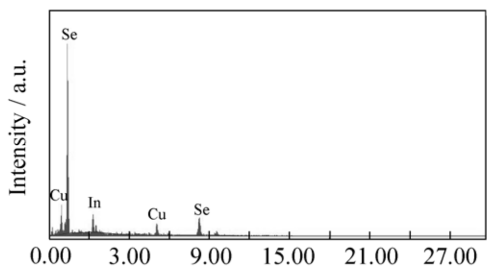

Fig. 2 EDS pattern of the $CuInSe_2$ film of the 17th experiment.

The XRD pattern of the $CuInSe_2$ film after annealing at 500°C for 30 min of the 18th experiment is shown in Fig. 4, which reveals that this film contains not only the $CuInSe_2$ phase but also the $Cu_{2-x}Se$ phase. The $CuInSe_2$ phase has a structure of chalcopyrite, and the structure of the $Cu_{2-x}Se$ phase is sphalerite. These two crystal structures have almost the same XRD peaks of (112), (220) or (204), and (116) or (312) planes. The atomic ratio of Cu, In, and Se in this film is 1:2.16:0.97 determined by ICP.

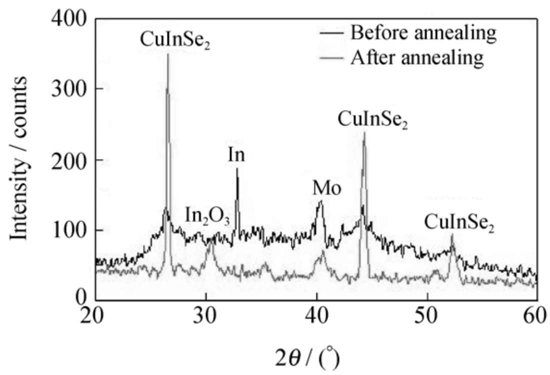

Fig. 3 XRD patterns of the $CuInSe_2$ film of the 17th experiment before and after annealing in vacuum at 500°C for 30 min.

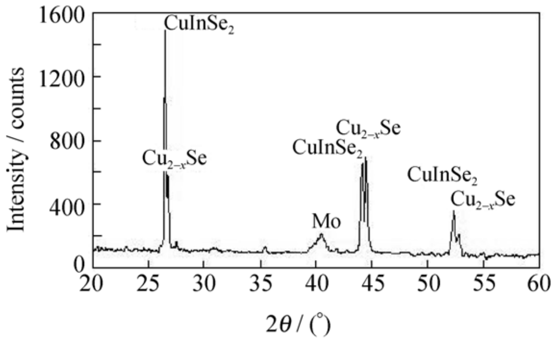

Fig. 4 XRD pattern of the $CuInSe_2$ film of the 18th experiment after annealing at 500°C for 30 min.

The integrated intensity, *i.e.*, the area inside the peak, of the (112) XRD peak from the $CuInSe_2$ phase in 18 experimental samples is listed in Table 3. It can be seen that the samples of the 3rd and the 16th experiments contain no $CuInSe_2$ phase and the sample of the 2nd experiment has the maximum amount of the $CuInSe_2$ phase. The XRD pattern also displays that the $CuInSe_2$ thin film generally exhibits a growth with a <112> preferred orientation, which is desired for the application in solar cells because it has the least lattice mismatch with CdS thin film grown on its surface. Table 3 also depicts the ratio of signal to noise, *S*/*N*, for the 18 experiment samples, which is defined as:

$$S/N = -10\lg[\mathrm{MSD}],$$

where MSD is the mean square deviation and is equal to $\sum_{i=1}^{n}\left(\frac{1}{y_i}-m\right)^2/n$, y_i is the integrated intensity of the (112) XRD peak from the $CuInSe_2$ phase, m is the mean value and is equal to zero; n is the number of each experiment and is equal to 3 in the present study. The more the value of y_i, the better the quality of the $CuInSe_2$ film; therefore, a relatively large value of *S*/*N* is expected. From the orthogonal array for the experiments (Table 2) and the signal-to-noise ratio, *S*/*N*, of each experiment (Table 3), the signal-to-noise ratio response for each control factor at each factor level can be calculated and is shown in Table 4, which is the average of all *S*/*N* ratios of a control factor at a given level. Fig. 5 depicts the *S*/*N* response for each factor level. The larger the *S*/*N* ratio, the larger the contribution of one control factor at that level for the quality of the $CuInSe_2$ film. Therefore, the optimum parameters for the $CuInSe_2$ film electrodeposition are A_2, B_2, C_2, D_2, E_1, F_1 (or F_2), G_2, and H_1, as shown in Table 4. Moreover, the larger the slope of the connected line of *S*/*N* ratios, the larger the effect of the control factor on the $CuInSe_2$ film electrodeposition, therefore, the TEA amount (F), $InCl_3$ concentration (D), and current density (B) are the parameters with relatively large effect on the electrodeposition of the $CuInSe_2$ thin film.

Table 3. Integrated intensity of the (112) XRD peak from the $CuInSe_2$ phase and signal-to-noise ratio for 18 experiments

No.	(112) XRD peak integrated intensity /counts	*S*/*N*
1	62.1	35.8618
2	165	44.3497
3	0	0.0000
4	17.3	24.7609
5	20.5	26.2351
6	85.3	38.6190
7	154.2	43.7617
8	30.4	29.6575
9	52.7	34.4362
10	97.5	39.7801
11	23.6	27.4582
12	63.9	36.1100
13	123.7	41.8474
14	37.6	31.5038
15	60.4	35.6207
16	0	0.0000
17	67.5	36.5861
18	155.2	43.8178
Mean *S*/*N*	—	31.6892

Table 4. Signal-to-noise ratio response for each control factor at each factor level

Level	A	B	C	D	E	F	G	H
Level 1	30.85	23.89	31.62	32.45	36.84	36.45	27.36	35.16
Level 2	32.52	32.14	32.63	39.35	28.42	36.44	39.79	31.12
Level 3	—	23.94	31.43	23.26	29.81	22.18	27.92	28.79

Table 5 shows the ANOVA for the result of 18 experiments for the electrodeposition of the $CuInSe_2$ thin film. In Table 5, SS, *F*, *V*, and ρ represent the sum of squares owing to variation about the mean, the degree of freedom, the sum of squares per degree of freedom (V=SS/F), and contribution percentage of each factor ($SS_{factor}/SS_{total}\times 100\%$), respectively. The result of ANOVA shows that the control factor F (TEA amount), D ($InCl_3$ concentration), and B (current density) have the contribution percentages of 24.66%, 23.70%, and 22.00%, respectively, and the control factor H (deposition time), C ($CuCl_2$ concentration), and A (annealing temperature) have the contribution percentages of only 3.78%, 0.17%, and 0.38%, respectively. From the results of the analyses of mean and variance, it can be seen that the factors with relatively large effect on the $CuInSe_2$ film quality are the TEA amount, $InCl_3$ concentration, and current density; the H_2SeO_3 concentration and pH value are the two factors with relatively small effect, and the effects of deposition time, $CuCl_2$ concentration, and annealing temperature are very small.

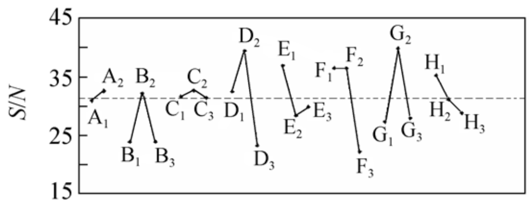

Fig. 5. *S/N* response for each factor level.

Table 5. ANOVA for the result of 18 experiments for the electrodeposition of the $CuInSe_2$ thin film

Factor	SS	*F*	*V*	ρ / %
A	12.57	1	12.57	0.38
B	726.36	2	363.18	22.00
C	5.75	2	2.87	0.17
D	782.27	2	391.14	23.70
E	244.36	2	122.18	7.40
F	813.95	2	406.98	24.66
G	591.01	2	295.51	17.90
H	124.86	2	62.43	3.78
Total	3301.13	15	—	100.00

From the view point of electrochemistry, the reduction reactions and the related electrode potentials for Cu, In, and Se can be written as below [22].

$$Cu^{2+}+2e \rightarrow Cu \quad (1)$$

$$E_{Cu}=0.34+0.0295\lg\left(\frac{a_{Cu2+}}{a_{Cu}}\right) \quad (2)$$

$$In^{3+}+3e \rightarrow In \quad (3)$$

$$E_{In}=-0.34+0.0197\lg\left(\frac{a_{In3+}}{a_{In}}\right) \quad (4)$$

$$H_2SeO_3+4H^{+}+4e \rightarrow HSeO_2^{-}+4H^{+}+4e+OH \rightarrow Se+3H_2O \quad (5)$$

$$E_{Se}=0.74+0.0148\lg\left(\frac{a_{HSeO_2^-}}{a_{Se}}\right)-0.0433\text{pH} \quad (6)$$

where a_{Cu2+}, a_{In3+}, and $a_{HSeO_2^-}$ are the ion activities in the solution; a_{Cu}, a_{In}, and a_{Se} are the atom activities in the electrodeposits; and the electrode potentials E_{Cu}, E_{In}, and E_{Se} are referred with respect to the normal hydrogen electrode.

It can be seen from Nernst equations (2), (4), and (6) that under general condition, the order of reduction trend for Cu, In, and Se is Se>Cu>In. For obtaining the $CuInSe_2$ film that has an atomic ratio of 1:1:2 for Cu, In, and Se, the activities a_{Cu2+}, a_{In3+}, and $a_{HSeO_2^-}$ (*i.e.* the concentration of Cu^{2+}, In^{3+}, and $HSeO_2^-$) and the pH value of the solution should be adjusted to optimum values. In the present study, the ranges of $CuCl_2$, $InCl_3$, and H_2SeO_3 concentrations is 5-15, 25-75, and 15-50 mM, respectively, and the pH value of the solution ranges from 1.5 to 1.8. Moreover, TEA is added to the solution to control the reduction rate of Cu, which ranges from 0 to 5 mL.

For the electrodeposition of the $CuInSe_2$ thin film on Mo surface in addition to the thermodynamics stated above, the kinetics also needs to be considered. In addition to the electrode potential calculated by the Nernst equation, there are some overpotentials occurring in the electrodeposition process. They include electron transfer, ohmic resistance, ion diffusion, and hydrogen reduction overpotentials. These overpotentials can be changed by the current density of electrodeposition. The present study used a current density ranging from 5 to 9 mA/cm^2.

The results of 18 experiments show that the optimum condition for the $CuInSe_2$ electrodeposition is as the following: current density, 7 mA/cm^2; $CuCl_2$, 10 mM; $InCl_3$, 50 mM; H_2SeO_3, 15 mM; TEA, 0 mL; and pH value, 1.65 (as shown in Table 6). The concentration of $InCl_3$ is larger than those of $CuCl_2$ and H_2SeO_3. This is consistent with the expectation of thermodynamics. In other words, it is necessary to increase the concentration of $InCl_3$ for the electrode potential of E_{In} to near E_{Cu} and to increase the concentration of H_2SeO_3 for the Se atoms to be double the amount of Cu atoms. The optimum amount of current density is 7 mA/cm^2, which is also consistent with the result published in Ref. [9].

Table 6. Optimum parameters for the $CuInSe_2$ film electrodeposition

Factor	Optimum value
A	500
B	7
C	10
D	50
E	15
F	0
G	1.65
H	10

4. Conclusion

The $CuInSe_2$ thin film for solar cells can be synthesized by electrodeposition in one plating bath consisting of $CuCl_2$, $InCl_3$, and H_2SeO_3. The optimum electrodeposition parameters are as follows: current density, 7 mA/cm^2; $CuCl_2$, 10 mM; $InCl_3$, 50 mM; H_2SeO_3, 15 mM; TEA, 0 mL; pH value, 1.65; and deposition time, 10 min. The three factors of TEA, $InCl_3$, and current density have relative large effects and the effects of another three factors of deposition time, $CuCl_2$, and annealing temperature are very small. Although the formation of the film is relatively less sensitive to the annealing temperature, only 400 and 500°C in this study, the annealing treatment is necessary for the film after formation in the electrodeposition process. After annealing in vacuum at 500°C for 30 min, the defects in the $CuInSe_2$ film will be reduced and the crystallinity of the $CuInSe_2$ film will be promoted.

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