Electrochemical deposition of $CuInS_2$ thin films

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Abstract

Chalcopyrite thin films were one-step potentiostatically deposited onto stainless steel plates from aqueous solution containing $CuSO_4$, $In_2(SO_4)_3$ and $Na_2S_2O_3$.The ratio of (In^{3+}:Cu^{2+}) which involved in the solution and The effect of cathodic potentials on the structural had been studied. X-ray diffraction (XRD) patterns for deposited films showed that the suitable ratio of (In^{3+}:Cu^{2+}) =6:1, and suitable voltage is -0.90 V versus (Ag/AgCl) reference electrode.

Key words
$CuInS_2$,
Electrical properties,
Solar cells,
chalcopyrite

Article info
Received: Oct. 2010
Accepted: Sep. 2011
Published: Oct. 2011

الترسيب الكهروكيميائي لأغشية $CuInS_2$ الرقيقة

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الخلاصة

تم في هذا البحث تحضير غشاء رقيق من $CuInS_2$ بواسطة الترسيب الكهربائي على صفائح من الستيلس ستيل من محلول مائي يحتوي على المواد التالية $In_2(SO_4)_3$, $CuSO_4$، $Na_2S_2O_3$. تم دراسة نسبة الايونين (In^{3+}/Cu^{2+}) المناسبة الموضوعة في المحلول وكذلك الجهود المسلطة وتاثيرها على تركيب الغشاء المترسب. حيود الاشعة السينية للاغشية المترسبة اظهرت ان النسبة (In^{3+}:Cu^{2+}) المناسبة =6:1 وان الفولتية المناسبة هي ٠,٩- V عن قطب (Ag/AgCl) القياسي.

Introduction:

The ternary compound $CuInS_2$ with chalcopyrite structure has attracted considerable attention as a suitable material to fabricate low-cost, efficient solar cells. This is mainly due to its direct band gap energy of 1.55 eV at room temperature. [1].

Many deposition methods have been developed for the preparation of $CuInS_2$ thin films, such as sulfurization of eletrodeposited Cu-In precursor, wet chemical route, chemical bath deposition, chemical vapor deposition, spray pyrolysis, ion plating, ion layer gas reaction (ILGAR) and co-evaporation [2]. Among the various deposition techniques, electro deposition is the most suitable for the commercial and large scale application. Electro deposition is an attractive technique and has widely been employed for the deposition of elemental, binary, intermetallic, ternary or even more complex compound and alloy thin films. It is an isothermal process mainly controlled by electrical parameters which are easily adjusted to control thickness, microstructure and composition [3].

The aim of this work is to study the voltage scan of H_2O decomposition and the voltage scan of electrodeposition for Cu, In and S; The structural properties for electrodeposited Cu-In-S films for different molar ratio (Cu/In) and different voltages have been also studied.

Experimental

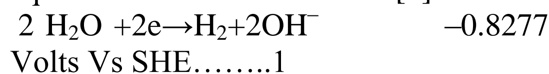
A three electrode-cell was used, where Ag/AgCl as the reference electrode, stainless steel (10 cm^2) as the working

electrode (cathode) and a graphite rod as the counter electrode (anode). The substrates and the counter electrode were cleaned with acetone, sodium hydroxide and followed by deionized water using ultrasonic bath. At first each component (Cu, In and S) electrodeposited from 4 mM $CuSO_4$, 4 mM $In_2(SO_4)_3$ and (400mM) $Na_2S_2O_3{:}5H_2O$ respectively. Then electrodeposition membranes from bath consisted of (3 mM) $CuSO_4$, (1.5-9 mM) $In_2(SO_4)_3$ and (400mM) $Na_2S_2O_3{:}5H_2O$. The pH was adjusted to 2 using Tartaric acid and then to 1.50 using sulfuric acid. Different cathodic voltage were supplied (-0.6 ,-07 and -0.9 V vs Ag/AgCl). The solution was stirred until the films electrodepositon. The films were electrodeposited at room temperature .

The deposited films were rinsed with deionized water and kept for further characterization. The films were analyzed using a Philips PZ 3710 x-ray diffractometer using monochromatic $CuK_{\alpha 1}$ radiation (λ=1.5406 A˚) in a scanning angle range of 25-60◦.

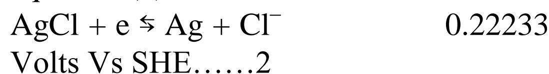
Results and Discussion

Fig (1) shows the J-V characteristic of Hydrogen evaluation occurs at (-1.040 V, vs Ag/AgCl) which respect to the equation of half cell reaction: [4]



$2\,H_2O + 2e \rightarrow H_2 + 2OH^-$ –0.8277 Volts Vs SHE……..1

It is clear that the Ag/Agcl reference electrode voltage =1.040-0.8277=0.212 mV. This value is very close to that at equation (2)



$AgCl + e \leftrightharpoons Ag + Cl^-$ 0.22233 Volts Vs SHE……2

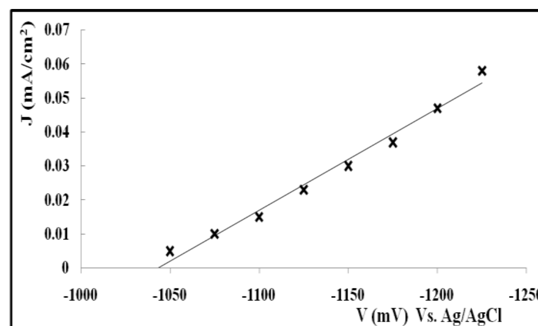


Fig. (1) the J-V characteristic of Hydrogen evalution from H_2O decomposition at 25°C, pH =1.5, (Scan Rate = 2 mV/s).

Fig. (2) showed the J-V characteristic of (Sulfur) electrodeposition from 400mM $Na_2S_2O_3$ on stainless steel substrate at 25°C, pH =1.5 (Scan Rate = 2 mV/s). Sulfur anions prepared from the following reaction:

$S_2O_3^{2-} + 6H^+ + 4e \rightarrow 2S + 3H_2O$ …3

The sodium thaio sulfate play as a reducing agent.

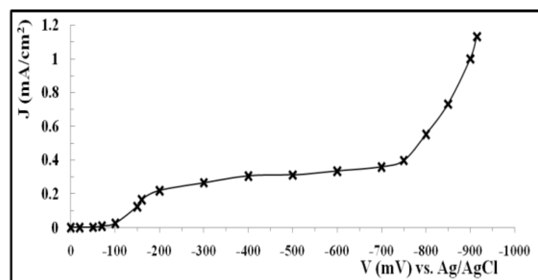
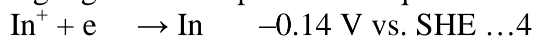
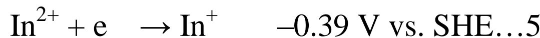


Fig. (2) the J-V characteristic of (Sulfur) electrodeposition from 400mM Na_2SO_3 on SS Substrate at 25°C, pH =1.5 (Scan Rate = 2 mV/s).

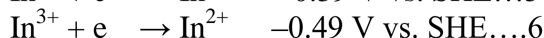
Fig. (3) Shows the J-V characteristic of (In) electrodeposition from 4 mM Indium Sulfate. Three peaks can noticed from it at -340,-590 and -690 mV versus Ag/AgCl with respect to the equations:



$In^+ + e \rightarrow In$ –0.14 V vs. SHE …4



$In^{2+} + e \rightarrow In^+$ –0.39 V vs. SHE…5



$In^{3+} + e \rightarrow In^{2+}$ –0.49 V vs. SHE….6

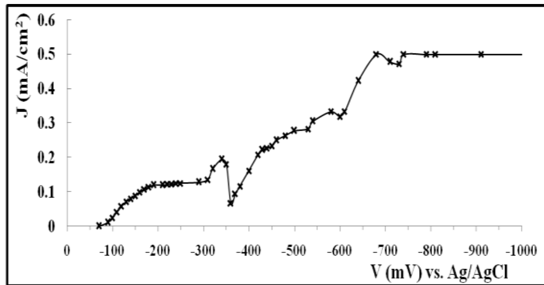


Fig. (3) the J-V characteristic of (In) electrodeposition from 4 mM Indium Sulfate on SS Substrate at 25°C, pH =1.5 (Scan Rate = 2 mV/s).

Fig.(4) shows the J-V characteristic of (Cu) electrodeposition from 4 mM Copper Sulfate on stainless steel Substrate at 25°C, pH=1.5.
Fig. (3) and (4) show that at voltage -700 the rate of (Cu) deposition is much greater than for (In) and it was not stable. While at -900 the rate of deposition of two is stable but it was still great. So the concentration of the composition must be chosen as ($CuSO_4/In_2(SO_4)_3<1$).
This results agree with Raza et al (1996) who used 0.01M $InCl_3$ and 0.001 M $CuCl_2$ to electrodeposited $CuInS_2$ film [5], Kopach et al (2001) used 0.9 mM CuCl,4.5 mM $InCl_3$ and 1.5 mM SeO_2 to electrodeposited $CuInSe_2$ $_{film}$ [6], Chraibi et al (2001) used 3mM of Cu^{2+}, 10mM of In^{3+}, 10mM of $HSeO_2$ to electrodeposited $CuInSe_2$ film [7] and Meglali et al (2008) used 10 mM of $CuCl_2$, 20mM of $InCl_3$ and 40 mM of SeO_2 to electrodeposited $CuInSe_2$ film [8]

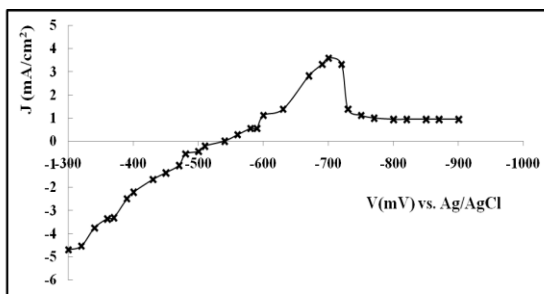


Fig. (4.) The J-V characteristic of (Cu) electro deposition from 4 mM Copper Sulfate on SS Substrate at 25°C, pH=1.5 (Scan Rate = 2 mV/s).

Fig (5) shows the variation of current density with time at electro deposition of $CuInS_2$ at -900 mV versus Ag/AgCl on SS plate. From this figure can notice that the current at the beginning decreasing with time and then being stable.

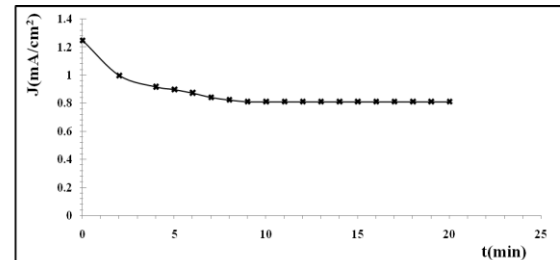


Fig. (5) The relation between J (mA/cm^2) versus the time in minute for $CuInS_2$ at -0.9V vs Ag/AgCl.

Current-time dependence due to mass transport in term of diffusion causes the concentration gradient in the vicinity of the electrode surface. This involves a gradual expansion of the diffusion layer associated with the depletion of the reactant and hence decreases the slope of the current profile. [9].
Fig. 6 shows that the X-ray diffraction for the stainless steel (314) plate which used as a substrate to deposited thin film on it. Table (1) shows the experiment and the standard peaks for Fe-Ni-Cr crystal and their intensities, it shows a perfect identical between them because the domain contain of SS-314 are Fe, Ni and Cr (see Table 2).

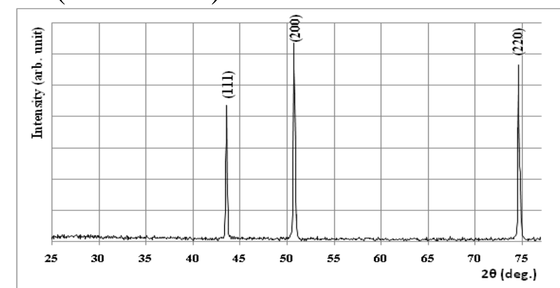


Fig.(6) XRD for stainless steel plate which uses as a substrate.

Table (1) The experiment peak for uses SS plate and the standard peaks for Fe-Ni-Cr crystal and their intensities [10]

2θ exp.	d Exp. (A°)	Int. %	d Std. (A°)	Int. %	hkl
43.592	2.075	67	2.08	100	111
50.766	1.797	100	1.80	45	200
74.616	1.271	97	1.27	26	220

Table 2 Chemical composition of stainless steel -314 alloy %.

Element	Fe≈	C max	Mn max	Si max	P max	S max	Cr	Ni
Wt.%	48-54	0.25	2.00	1.5-3	0.045	0.03	23-26	19-22

Fig. (7) shows XRD for thin film electrodeposited on SS from solution contain Cu:In molar ratio (1:1) for different applied voltage versus Ag/AgCl electrode. At -0.6 V and -0.7 V for electrodeposited film (Fig. 7-a and b) only the substrate peaks were observed but at (b) the intensities higher than at (a) which refers to Cu electrodeposited which peaks identical with these, because at this voltage the Cu anions was electrodeposited at high rate (see Fig. 4). At -0.9 V(Fig. 7-c) we can see two peaks for Covellite (CuS) phase.

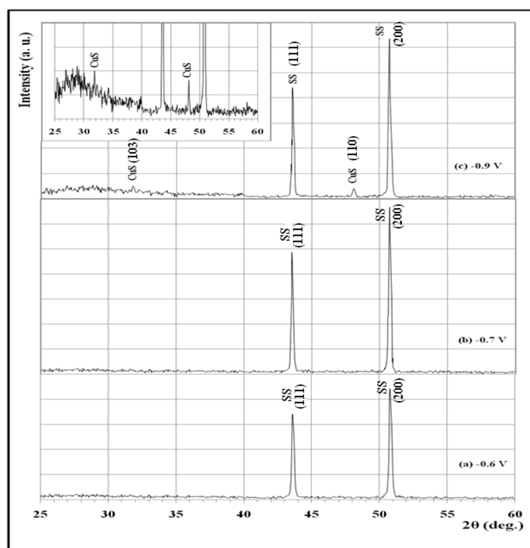


Fig. (7) XRD for thin films on SS, annealed at 200°C from solution contain Cu:In molar ratio (1:1) for different applied voltage (a) -0.6V (b) -0.7V (c) -0.9V versus Ag/AgCl electrode.

Fig. (8) Shows XRD for thin film electrodeposited on SS plate from solution contain Cu:In molar ratio (1:2) for different applied voltage versus Ag/AgCl electrode (-0.6, -0.7 and -0.9 V).

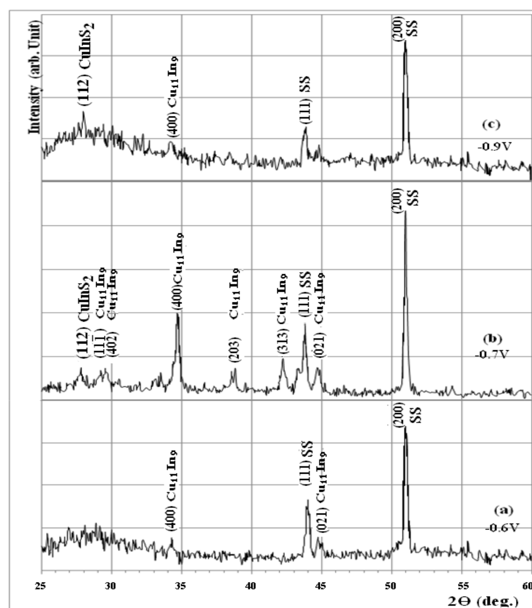
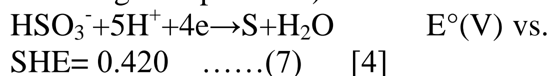


Fig. (8) XRD for thin films on SS, annealed at 200°C from solution contain Cu:In molar ratio (1:2) for different applied voltage (a) -0.6V (b) -0.7V (c) -0.9V versus Ag/AgCl electrode.

Fig. (8-a) shows small intensities peaks for $Cu_{11}In_9$ appear at 2θ =34.28^0 and 44.74 ^{0} with hkl{(400) and (021)} respectively.
In Fig. (8-b) the substrate peaks were noticed but theirs intensities higher than at Fig.(8-a) correspond of Cu phase, in addition to a small peak for $CuInS_2$ with hkl (112) located at 2θ = 28.0126, and others for $Cu_{11}In_9$ appeared at 2θ=29.4, 29.6, 34.75, 38.77, 42.22 and 44.74 with hkl{($11\bar{1}$), (402), (400), (203), (313), and (021)} respectively. The results in (a) and (b) shows deficiency samples from sulfur because no hydrogen evaluation from cathode at these voltage (see Fig.2).
In Fig. (8-c) the peaks correspond to Cu-In alloy are disappear and the peak

correspond to (112) of $CuInS_2$ at 2θ = 28.0126 appear most clear than at others, this result correspond to hydrogen evaluation from cathode and then prepare sulfur anions by chemical reaction between hydrogen and HSO_3^- anions (see Fig. 2. sulfur more electrodeposited at more negative potential)



$HSO_3^- + 5H^+ + 4e \rightarrow S + H_2O$ E°(V) vs. SHE= 0.420 ……(7) [4]

These results are in agreement with Yunbin He (2003) [11], he studied the Influence of the H_2S flow on the properties of $CuInS_2$ Thin Films prepared by Reactive Sputter Deposition and found that at low flow Cu-In alloy phases coexisting in the films. When the H_2S flow during sputtering increased the secondary Cu-In phases were suppressed, and nearly pure $CuInS_2$ phase films were obtained.

Fig. (9) shows the XRD for thin film electrodeposited from solution contain Cu:In molar ratio (1:6) at -0.9V versus Ag/AgCl electrode on SS substrate.

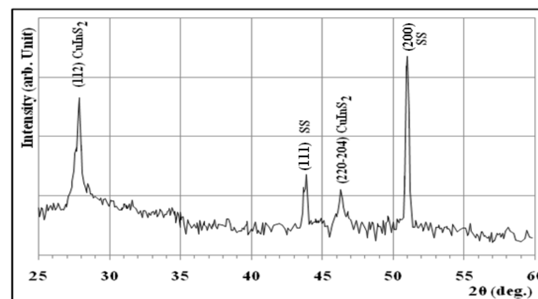


Fig. (9) XRD for thin film electrodeposited from solution contain Cu:In molar ratio (1:6) at -0.9V versus Ag/AgCl electrode.

The pattern included two peaks at 2θ equal to (27.875° and 46.402°) referred to (112) and (220-204) direction of chalcopyrite $CuInS_2$ respectively. This figure confirms that the preferential orientation is in the (112) direction.

These results are in agreement with JCPDS data [10], Mere et al (2003) [12], Yunbin He (2003) [11] , Hou and Choy (2004) [13], Aksay (2005) [14], Akaki et al (2007) [15], Rabeh et al (2009) [16].

Table (3) Comparison of observed and standard (d) values for different phases observed in films deposited in different voltages and Cu:In molar ratios[10].

Cu/In	Supplied voltage vs. Ag/AgCl	Peak 2θ (deg.)	Exp. d (A°)	Int.%	Stan. d (A°)	Int.%	phase	Plane (h k l)	JCPDS Card no.
1:1	-0.60	43.601	2.0758	-	2.08	-	FeNiCr	(111)	33-397
		50.797	1.7973	-	1.80	-	FeNiCr	(200)	33-397
	-0.70	43.504	2.0802	-	2.08	- 100	FeNiCr +Cu	(111) (111)	33-397 4 - 836
		50.737	1.7993	-	1.80	- 46	FeNiCr +Cu	(200) (200)	33-397 4 - 836
	-0.90	43.549	2.0782	-	2.08	100	FeNiCr	(111)	33-397
		50.746	1.7990	-	1.80	80	FeNiCr	(200)	33-397
		31.790	2.8148	100	2.81	90	CuS	(103)	6- 464
		48.124	1.8907	80	1.90	100	CuS	(110)	6- 464
1:2	-0.60	43.996	2.0581	-	2.08	-	FeNiCr	(111)	33-397
		50.971	1.7916	-	1.80	-	FeNiCr	(200)	33-397
		34.278	2.6160	98	2.607	50	$Cu_{11}In_9$	(400)	41-883
		44.744	2.0254	100	2.047	10	$Cu_{11}In_9$	(021)	41-883
	-0.70	43.829	2.0655	-	2.08	-	FeNiCr	(111)	33-397
		51.065	1.7885	-	1.80	-	FeNiCr	(200)	33-397
		27.785	3.2107	38.3	3.198	100	$CuInS_2$	(112)	27-159
		29.400	3.0379	31.6	3.034	80	$Cu_{11}In_9$	(11-1)	41-883
		29.605	3.0174	32.6	3.016	80	$Cu_{11}In_9$	(402)	41-883
		34.751	2.5814	100	2.607	50	$Cu_{11}In_9$	(400)	41-883
		38.775	2.3223	37.2	2.381	20	$Cu_{11}In_9$	(203)	41-883
		42.22	2.1404	48.5	2.136	100	$Cu_{11}In_9$	(313)	41-883
		44.736	2.0257	35.2	2.047	10	$Cu_{11}In_9$	(021)	41-883
	-0.90	43.906	2.0621	-	2.08	-	FeNiCr	(111)	33-397
		50.972	1.7916	-	1.80	-	FeNiCr	(200)	33-397
		27.952	3.1919	100	3.198	100	$CuInS_2$	(112)	27-159
		34.244	2.6185	55	2.607	50	$Cu_{11}In_9$	(400)	41-883
1:6	-0.90	43.866	2.0622	-	2.08	-	FeNiCr	(111)	33-397
		50.999	1.7789	-	1.80	-	FeNiCr	(200)	33-397
		27.875	3.1981	100	3.198	100	$CuInS_2$	(112)	27-159
		46.402	1.955	36	1.952	25	$CuInS_2$	(204,220)	27-159

Table (3) shows the comparison of observed and standard (d) values (from JCPDS) for different phases observed in films deposited in different voltages and different Cu:In molar ratios.

The grain size was calculated by Scherrer's formula:

$$b = \frac{0.89\,\lambda}{\Delta(2\theta).\cos(\theta)} \quad \dots(8)$$

Where λ=0.15406 nm for $CuK_{\alpha 1}$, $\Delta(2\theta)$=the full half width= 0.3023 deg. = 0.00527 rad. And θ=27.9/2=13.95°

$$b = 26.8\ nm$$

Electrodeposition normally leads to small particle size, mainly because it is a low temperature technique [17] .

Lattice parameters (a) and (c) were calculated from X-ray d-spacings according to equation

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad \dots\dots\dots(9)$$

Where h, k, and l refer to the Miller indices of individual reflections. The d-spacing of the (220) reflection was used to calculate (a)

$$\frac{1}{(1.955)^2} = \frac{2^2+2^2}{a^2} + \frac{0^2}{c^2} \Rightarrow a = 0.5530\ nm$$

And the d-spacing of the (112) reflection was used, with the calculated lattice parameter a, to determine c.

$$\frac{1}{(0.31981)^2} = \frac{1^2+1^2}{(0.553)^2} + \frac{2^2}{c^2} \Rightarrow c = 1.111625\ nm$$

This method used by Banger et al (2002) [18].

The lattice parameters, the distortion parameter x (where x= 2–c/a), (given that a hypothetical c/a ratio of 2 would result in the absence of any tetragonal distortion) and the anion displacement parameter u (where u = 0.25+x) are presented in Table (4).

Comparison of the data collected from the $CuInS_2$ film shows they are in good agreement with the JCPDS reference values for single-crystal $CuInS_2$.

Table(4) Comparison of the lattice parameters, c/a ratio, and the distortion parameter u of $CuInS_2$ with the JCPDS reference values[10] .

$CuInS_2$	a (nm)	c (nm)	η=c/2a	X(nm)	u (nm)
Exp. values	0.5530	1.1116	1.0051	0.010	0.240
JCPDS values [67]	0.5523	1.1141	1.0086	0.017	0.233

Conclusions

The chalcopyrite $CuInS_2$ films were successfully deposited on SS using electrochemical technique. The structural of electrodeposited films were studied for different precursor concentration and different applied voltage.

It was found that the ratio of precursor concentration play an important role to successfully electrodeposited chalcopyrite $CuInS_2$ films and the best molar ratio of In:Cu=6:1 in the solution to electrodeposited chalcopyrite $CuInS_2$ films.

It was found that the applied voltage is also an important role in electrodeposited of $CuInS_2$, and the best voltage is -0.9 V versus Ag/AgCl.

Electrodeposited $CuInS_2$ film have chalcopyrite structure with preferential orientation at (112) direction located at 2θ= 27.875°.

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