Structural and DC Electrical Properties of (CuI) Thin Film Prepared by Pulse Laser Deposition

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ABSTRACT

In this paper , Copper(I) Iodide (CuI) thin films were prepared by Pulsed Laser Deposition (PLD).The effect of different No. of laser pulse (200,500 and 800) on the structural and electrical properties were studied . The structure of all CuI films is tested using X-ray diffraction (XRD) the results were found to be polycrystalline of hexagonal structure with strong crystalline orientation at (111)plane. D.C measurements revealed that the electrical activation energy (Ea) decreases with increasing of pulse shoot of thin films. The Hall effect measurements confirmed that the CuI are P-type and the charge carriers concentration (n) were increased with increasing of pulse shoots .Also, it can observe that Hall mobility (μ_H) decreases with the increasing of pulse shoot for films.
Keywords :PLD technigue, CuI thin film , Al, Nd:YAG, PL

INTRODUCTION

C uI material is a p- type semiconductor[1] having a band gap of about 3.1 eV. The band gap is associated with promotion of a 3d electron to the 4s or 4p sub shell. This results in photoluminescence emission centred near the UV /vis transition [2]. CuI can be use for the order heterojunction, which can efficiently improve the exciton dissociation. Therefore the performance of CuI can be improved significantly with the application of metal oxides[3].

In recent years, wide band-gap semiconductors (WBSs) have been a great concern due to the promise applications in high-frequency high-power electronics and UV optoelectronic devices[4]. The operating characteristics of these devices depend critically on the physical properties of materials. In terms of p-n junction devices, the carrier mobility of p-type WBS materials as well as the n-type counterparts is one of the key factors affecting the efficiency of the CuI. However, it is not easy for most WBS

materials, such as GaN, SiC, and ZnO, to achieve stable high hole mobility, finding a high mobility p-type material is still one of the greatest challenges facing WBS researchers [5].   Properties of CuI play an important role in improving the solid state dye-sensitized solar cell(DSSC) [6]

In a solid state dye-sensitized solar cell the electrolyte is replaced with a p-type semiconductor or organic hole conductor materials avoiding problems such as leakage of liquid electrolytes[7]. Such as, CuI is considered to be a low-resistive and high

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mobility hole conductor compared to other hole conducting materials such as CuSCN, P3HT and spiro-OMeTAD. Therefore, the use of CuI as a hole collector in DSCs and other solar cells is highly beneficial owing to its capability of much lower hole- transport resistance which helps the efficient transport of holes away from Sb2S3. CuI can also be deposited from a solution of acetonitrile onto the photo anodes using a low-temperature deposition technique and hence without denaturing the dye
monolayers in the DSCs[8-9].

In this work ,use CuI film deposit by PLD method using Nd:YAG laser using pulsed Nd:YAG laser at 1064nm wavelength and   repetition rate 6Hz . The structure of the CuI are studied by X-ray diffraction (XRD) and the electrical testing of the film were investigated.

Experimental Work
PLD System
Thin films are prepared by pulsed laser deposition method (PLD), to ablate one or more targets illuminated a focused pulsed-laser beam.

The whole system consists of light route system, power supply system, the vacuum chamber up to 10^{-2} mbar, elementary or alloy targets are struck at an angle of (45^0) by a pulsed and focused laser beam. The atoms and ions ablated from the target(s) are deposited on substrates. etc. Mostly, the substrates are attached with the surface parallel to the target surface at a target-to-substrate distance of typically (2-10)cm. The light route system is installed into the hand piece, but power supply, controlling and cooling systems are installed into the machine box of power supply, as shown in figure (1) .
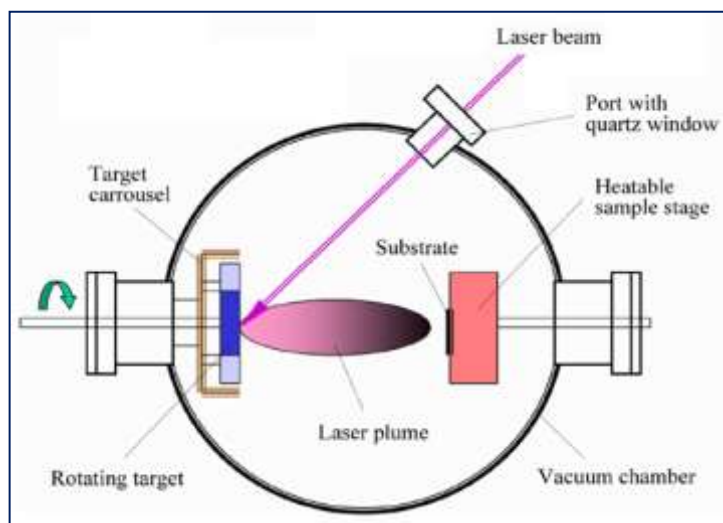
Figure(1):- Illustrate the PLD system .

Laser Source
Nd:YAG laser (HuafeiTongda Technology- DIAMOND- 288 pattern EPLS) is used for the deposition of CuI film on glass substrate . The system consists of light route system, power supply system, computer controlling system, cooling system, key switch etc. The light route system is

installed into the hand piece, but power supply, controlling and cooling systems are installed into the machine box of power supply.

Main Technical Parameters:
❖   Laser model: Q-switched
❖   Laser wavelength: (1064 and 532) nm.
Use wavelength 1064 nm
❖   Pulse energy: (100-1000) mJ.
Use energy 800 mJ
❖   Cooling method: inner circulation of water for cooling
❖   Power supply: 220V.
❖   Repetition frequency: (1,2,3,4,5 and 6) Hz
    Use frequency 6 Hz
❖   Pulse width : 10 ns for the wavelength= 1064 nm
❖   Pulse width : 7 ns for the wavelength= 532 nm
❖   Beam size = 0.4 mm

Deposition Chamber
    The shape of the deposition chamber is cylindrical made from high quality pyrex glass. Since the PLD system does not necessarily require ultra-high vacuum. Deposition chamber which include inside it the target, substrate and vacuum system.

Target preparation
    CuI powder from Nano shell company with purity of (99.99%). The mixing powder is pressed in to pellets (1.5)cm in diameter and(3)cm thick using hydraulic type (SPE CAC) as shown in figure (2a) under 5 Ton pressure for 7 min.
figure (2b) shows the pellet after pressing.

(a)   **(b)**

Figure (2):- (a)mead the target, (b)show the target after pressed of CuI thin films

Thickness measurement
    Film thickness measurements by optical interferometer method have been obtained. This method is based on interference of the light beam reflection from thin

film surface and substrate bottom. He-Ne laser(632.8nm) was used and the thickness was determined using the formula [10] :

$$t = \frac{\lambda}{2} \cdot \frac{\Delta X}{X}$$ …… (1)

Where (x) is the fringe width, (Δx) is the distance between two fringes and (λ)wavelength of laser light, as shown in figure (3).
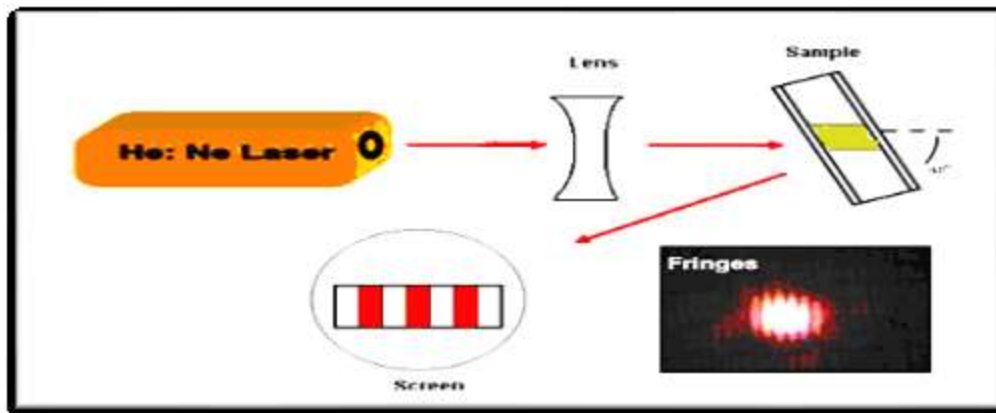

Figure (3):- The schematic diagram of the film thickness measurement.

Characterization Measurements

The structure of the CuI are studied by X-ray diffraction XRD were performed on a computer interface X-ray diffractometer (SHIMADZU JAPAN, XRD – 6000) with Cu Kα radiation (λ = 1.542 A°) was used and the electrical testing of the film were investigated by Hall effect and D.C conductivity. The electrical conductivity has been measured as a function of temperature for CuI films. The measurements have been done using sensitive digital electrometer type keithley (616) and electrical oven and Hall effect this is an important type of measurement to know much information that determines the efficiency of the semiconductor, also determine the semiconductor film type mobility and the charge concentration of the carriers need to be determined. A developed device of type (HMS-3000) was employed. This device was made available by the Ministry of Science and Technology.

Result and Desiccation
(X-Ray Diffraction Analysis)

Study the effect of different number of pulses (200, 500 and 800) of Nd:YAG laser on the crystal structure. The samples were prepared by PLD. Figure (4) shows the XRD patterns of the CuI powder at diffraction angles (10- 80). All the peaks are 100% phase matching with the CuI hexagonal phase of (ASTM) as shown in figure (5). The obtained result of XRD for CuI powder where listed in table (1).

The XRD patterns for CuI thin film deposited onto glass substrates at RT at different number of pulses (200, 500 and 800)where shown in figure (6). The different peaks can be assigned to polycrystalline hexagonal structure there are several peaks observed in the series of Bragg reflections in XRD pattern which are (111), (020), (202), (311) and (222) therefore, it is confirmed that the CuI thin film is a hole transport semiconductor. The peak of (111) plane have higher intensity compared to other peaks. Sharper peaks were obtained for film at higher pulses (800)

compared to (500, 200) pulses which has low intensity since it has the lowest thickness because the thickness of the CuI thin film increase as the number of laser pulse increase [11-12]. full-width at half-maximum (FWHM) of XRD lines calculated by using the Debye-Scherrer formula [13]:

————   Where *D* is the grain size of the crystallite, λ (1.54059) rays used, β is the broadening of diffraction line measured at the half of its intensity in radians and θ is the angle of diffraction[13].
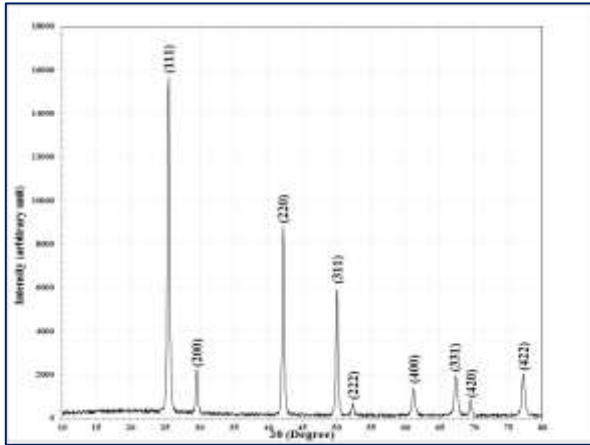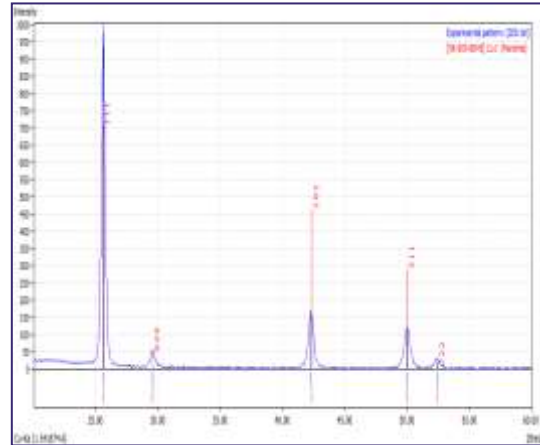

Figure (4) :- XRD spectra of CuI powder   **Figure (5) :- XRD spectra of CuI stander**
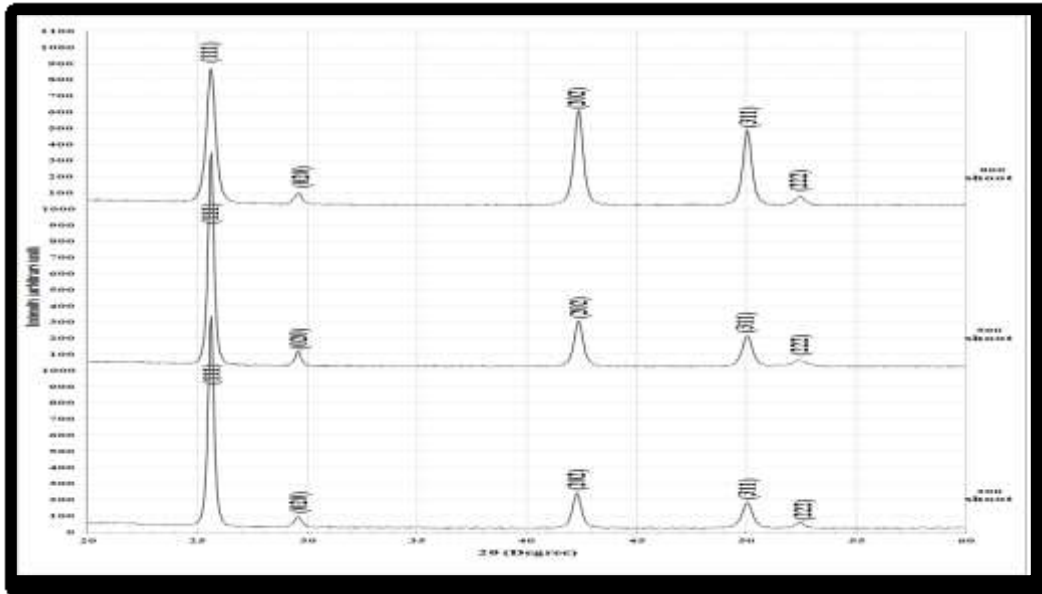

Figure (6):- X-ray diffraction pattern of CuI film at different No. of laser pulse (200,500 and 800)

Table (1):- illustrates the intensity(I) ,(2Θ) , (hkl) ,d and FWHM for CuI.

No. of pulse	2θ (Deg.)	FWHM (Deg.)	Intensity (arb unit)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl
200	25.5490	0.561	1303	3.484	14.5	3.4888	(111)
	29.6006	0.533	67	3.015	15.4	3.0213	(020)
	42.3219	0.535	218	2.134	15.9	2.1364	(202)
	50.0564	0.513	157	1.821	17.1	1.8219	(311)
	52.4201	0.538	36	1.744	16.5	1.7444	(222)
500	25.6007	0.623	1315	3.477	13.1	3.4888	(111)
	29.5913	0.499	86	3.016	16.5	3.0213	(020)
	42.3213	0.537	283	2.134	15.9	2.1364	(202)
	50.0574	0.518	191	1.821	16.9	1.8219	(311)
	52.4156	0.571	40	1.744	15.5	1.7444	(222)
800	25.5697	0.508	840	3.481	16.0	3.4888	(111)
	29.5827	0.509	70	3.017	16.2	3.0213	(020)
	42.3182	0.529	295	2.134	16.1	2.1364	(202)
	50.0516	0.512	231	1.821	17.1	1.8219	(311)
	52.4146	0.495	27	1.744	17.9	1.7444	(222)

Electrical measurement :-
a) D.C Conductivity :-

CuI film conductivity measured at room temperature ($\sigma_{R.T}$) were it found about (24.4, 13.3 and 3.2) $(\Omega.cm)^{-1}$ for sample No. of laser pulse (200, 500 and800), respectively .The variation of $\sigma_{R.T}$ is given in Table (2).

From figure (7) and Table (2) shows that $\sigma_{R.T}$ increases with increasing of No. of laser pulse.
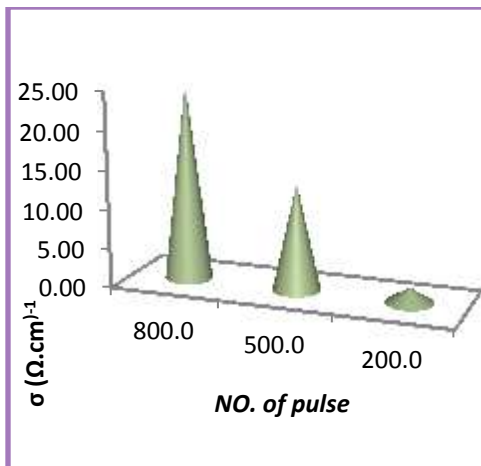

Figure (7) Variation of $\sigma_{R.T}$ versus No. of laser pulses for CuI *for CuI films*
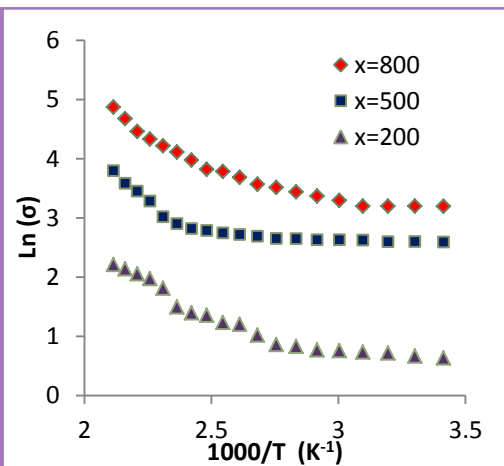
Figure (8): lnσ versus 1000/T for CuI at different laser pulses for CuI films

Table (2): D.C. conductivity parameters for CuI films at different pulse

No. of pulse	Ea1 (eV)	Range (K)	Ea2 (eV)	Range (K)	σ_{RT} $(\Omega.cm)^{-1}$
800	0.010	293-373	0.019	373-473	24.4
500	0.027	293-373	0.042	373-473	13.4
200	0.048	293-373	0.092	373-473	3.2

The plots of $\ln\sigma$ at versus $10^3/T$ for CuI films in the range (293-523) K at different pulse is shown in Figure (8). It is clear from this figure that there are two transport mechanisms, giving rise to two activation energies Ea_1 and Ea_2. The conduction mechanism of the activation energy (Ea_1) at the higher temperatures range (373-473)K in laser pulse 200 and(373-473)k in laser pulse (500,800) is due to carriers excitation into the extended states beyond the mobility edge and at the lower range of
temperatures(293-373), the conduction mechanism is due to carriers excitation into localized state at the edge of the band[14] .

Table (2) , figures (9) and (10) show the effect No. of laser pulse on activation energy Ea_1 for CuI films. It is clear that the activation energy Ea_1 and Ea_2 decrease with increasing of the thickness.

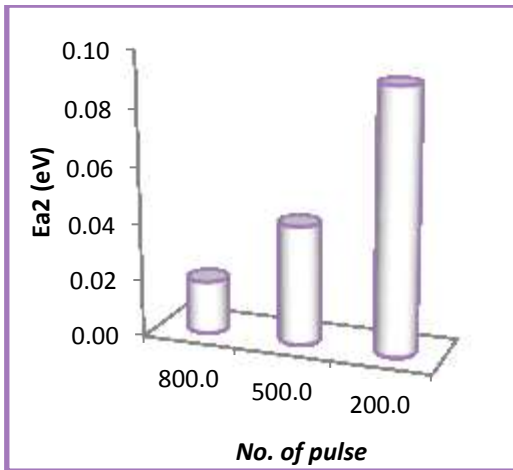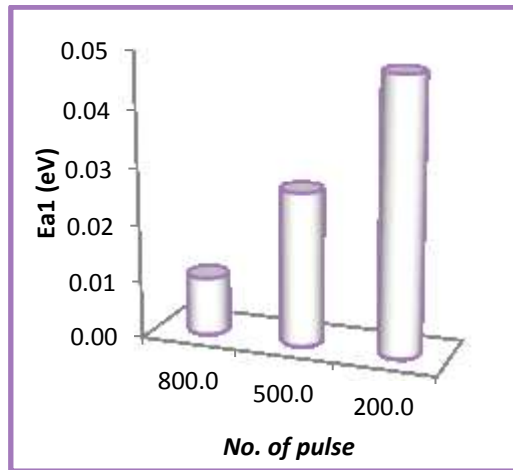Figure (9): Variation of Ea₂ for CuI
films at different laser pulse

Figure (10): Variation of Ea₁ for
CuI films at different laser pulse.

The Hall measurements is show in table (3) that includes Hall mobility, carrier type and concentration for CuI films at different No. of laser pulse were measured from Hall coefficient (R_H) data and the conductivity.

Hall measurements show that the CuI films are p-type i.e, the conduction is dominated by holes. The n_H was calculated by using the equation ——. Were the q electron charge. The carriers concentration was increased with increasing of No. of laser pulse as show in figure (11). It is also found that the mobility decreased with the increasing thickness of films due to increase the carriers concentration[13] as show in figure (12). The decrease of mobility comes from the inverse relation between μ_H and n_H. This is typical of many polycrystalline thin films and is due to the existence of potential barriers in the grain boundaries.

Table (3) : Hall effect measurements of (CuI).

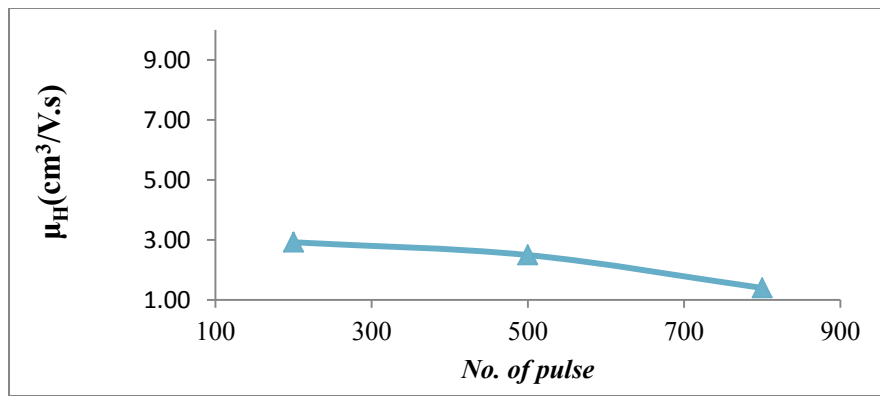| NO. Of pulse	σ_H $(\Omega.cm)^{-1}$	$R_H \times 10^3$ (cm^2/C)	n_H (cm^{-2}) $\times 10^{11}$	μ_H $(cm^2/V.s)$ $\times 10^3$	Type of conductance
200	13.64	4.360	14.33	2.920	p-type
500	55.26	3.820	16.36	2.494	p-type
800	83.53	1.207	51.78	1.393	p-type

Figure (11): Variation of N_H for CuI films at different laser pulse
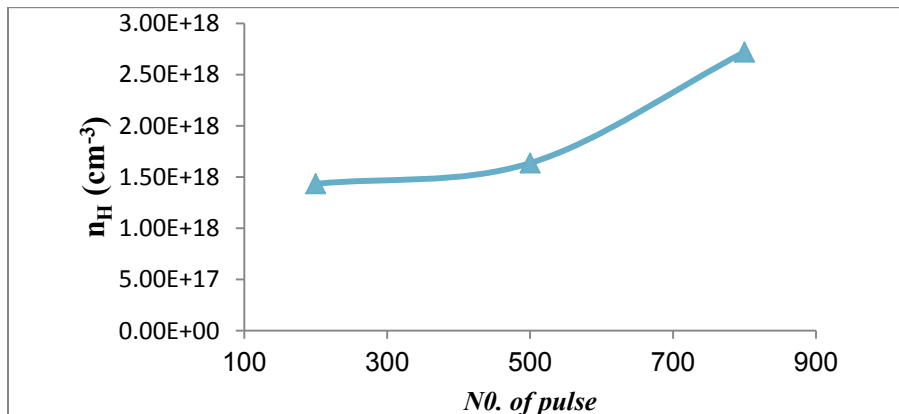

Figure (12): Variation of μ_H for CuI films at different laser puls

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CONCLUSION:

1-   All films have polycrystalline hexagonal structure.

2-   The hall effect measurement prove that CuI thin films had p-type . Also two activation energy. As the number of Nd:YAG laser pulse increase the n_H increase while the mobility μ_H decrease.

3-   All experimental works a proved that the materials are suitable as an initial stage for p-n junction and solar cells.

REFERENCES:-

[1].Y. Peng, N. Gross ,   A. Perumal, H. Faber, G. Vourlias, P. Patsalas, D. Bradley, and T. Anthopoulos, "Efficient organic solar cells using copper(I) iodide (CuI) hole transport layers " Appl. Phys. Lett. 106, 243302, (2015).

[2]. A. R. Kumarasinghe, W. R. Flavell, A. G. Thomas, A. K. Mallick, D. Tsoutsou, C. Chatwin, S. Rayner, P. Kirkham, and S. Warrenb, "Electronic properties of the interface between p - CuI and anatase-phase n - TiO_2 single crystal and nanoparticulate surfaces: A photoemission study" the jouranl of chemicalphysics 127, 114703-1, (2007).

[3].J. Safko, J. Kuperstock, S. McCullough, A. Noviello, J. Killarney, C.Murphy, H. Patterson, C. Bayse and R. Pike, "Network formation and photoluminescence in copper(I) halide complexes with substituted piperazine ligands †" Dalton Trans. 41, 11663– 11674 (2012).

[4].T. Tachikawa, M. Fujitsuka, and T. Majima, "Mechanistic insight into the TiO_2 photocatalytic reactions: design of new photocatalysts". The Journal of Physical Chemistry C, 111(14): p. 5259-5275, (2007).

[5].O. Ambacher, "Growth and applications of Group III-nitrides" Journal of Physics D: Applied Physics, 31, 20, (1998).

[6]. D. Chen, Y. Wang, Z. Lin, J. Huang, X. Chen, D. Pan, and F. Huang, "Growth Strategy and Physi cal Prope rties of the High Mobility P-Type CuI Crystal" American Chemical Society, 10, 2057-2060, (2010).

[7].M. Amalina, N. Rasheid and M. Rusop, "The Properties of Sprayed Nanostructured P-type CuI Film for Dye-Sensitized Solar CellApplication" Journal of Nanomaterials Volume 2012, Article ID 637637, 6, (2012).

[8].S. Gunes and N.S.Sariciftci, "Hybrid Solar Cell" inorganic chimica , 361, 581-588, (2008).

[9]. N. Dematage, E. Premalal and A. Konno, "Employment of CuI on Sb2S3 Extremely Thin Absorber Solar Cell: N719 Molecules as a Dual Role of a Recombination Blocking Agent and an Efficient Hole Shuttle" Int. J. Electrochem. Sci., 9 , 1729 – 1737, (2014).

[10].M. Caidi, A. Amassian, M. chakar and M. Kulishov "Pulsed Laser Deposition of PLZT film: structural and optical characterization" Applied Surface Science, Vol. 226, No. 4, P. 347-354, 2004.

[11].A. Kumarasinghe, W. Flavell, A. Thomas, A. KMallick, D. Tsoutsou, C. Chatwin, S. Rayner, P. Kirkham, and S. Warrenb, "Electronic properties of the interface between p - CuI and anatase-phase n - TiO_2 single crystal and nanoparticulate surfaces: A photoemission study" the journal of chemical physics, Vol. 127, P. 114703-1, 2007.

[12].H. Hoppe, S. Shokhovets, and G. Gobsch, "Inverse relation between photocurrent and absorption layer thickness in polymer solar cells" physica status solidi (RRL)-Rapid Research Letters, Vol. 1, No. 1, P. 40-42, 2007.

[13].. Sahan, "Properties of Nano Thin Film Composed of Nan Crystalline Zro_2Prepared by (SOL - GEL) Method" Eng. & Tech. Journal , Vol.32,Part (B), No.1, (2014).

[14].M. Amalina, A. Zainun, N. Rasheid and M. Rusop, "The electrical conductivity of copper (I) iodide (CuI) thin films prepared by mister atomizer" 5th BSME International Conference on Thermal Engineering, P. 128-131, (2012).