Direct observation of twinning domains in copper iodide thin film synthesized by magnetron sputtering of Cu thin layers at low temperature and iodine vapor

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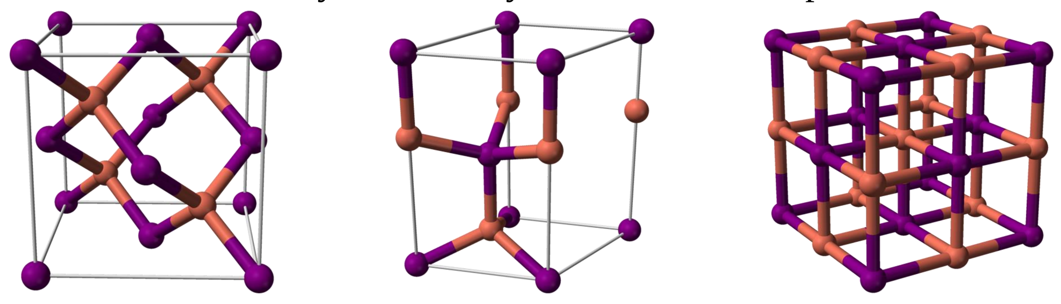
Introduction

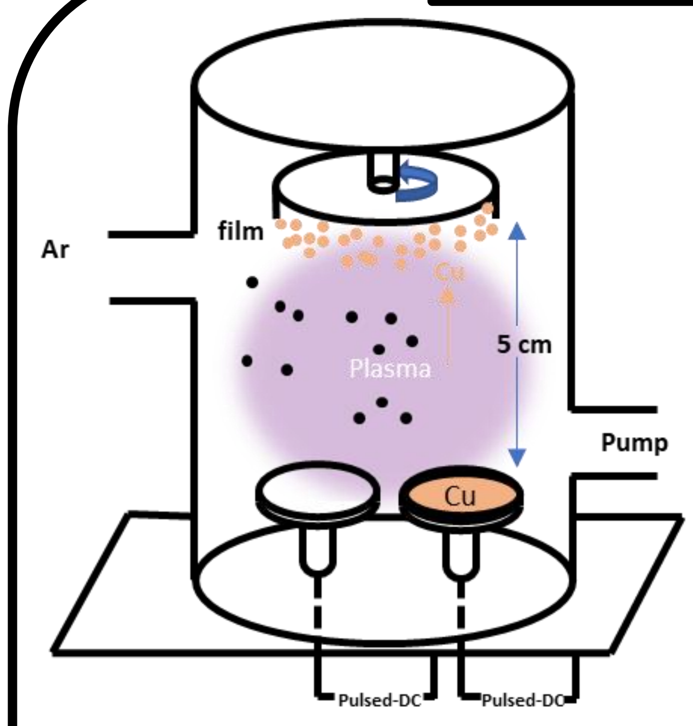
Copper (I) iodide (CuI) is attracting much attention for thin film photovoltaic application, due to promising applications in UV optoelectronic devices, wide band-gap semiconductors. It has enormous interest: elemental abundance, non-toxic, and inexpensive, *etc.*, [1], [2]. The Copper Iodide, CuI, is multipurpose compound elements that has several uses and has been found to be essential in the study of numerous materials. Copper Iodide is unique due to the fact that is scientifically verified to be an inorganic semiconductor and concurrently able to link up in chemical bonding with several other organic and inorganic ligands [3]. It has the property of exhibiting a broad bandgap semiconductor ≈ 3.1 Ev [4]. Three allotropic forms α, β, and γ are well known for CuI [5]. The γ-CuI allotrope (F-43m, a = 6.054 Å) is very promising as a transparent semiconductor. Therefore, transparent p-type semiconductors anticipated for further development of transparent electronics. In this work, thin films of CuI have been synthesized by the iodination of sputtered Cu coatings with iodine vapor to investigate the film properties and their optoelectronic performance.

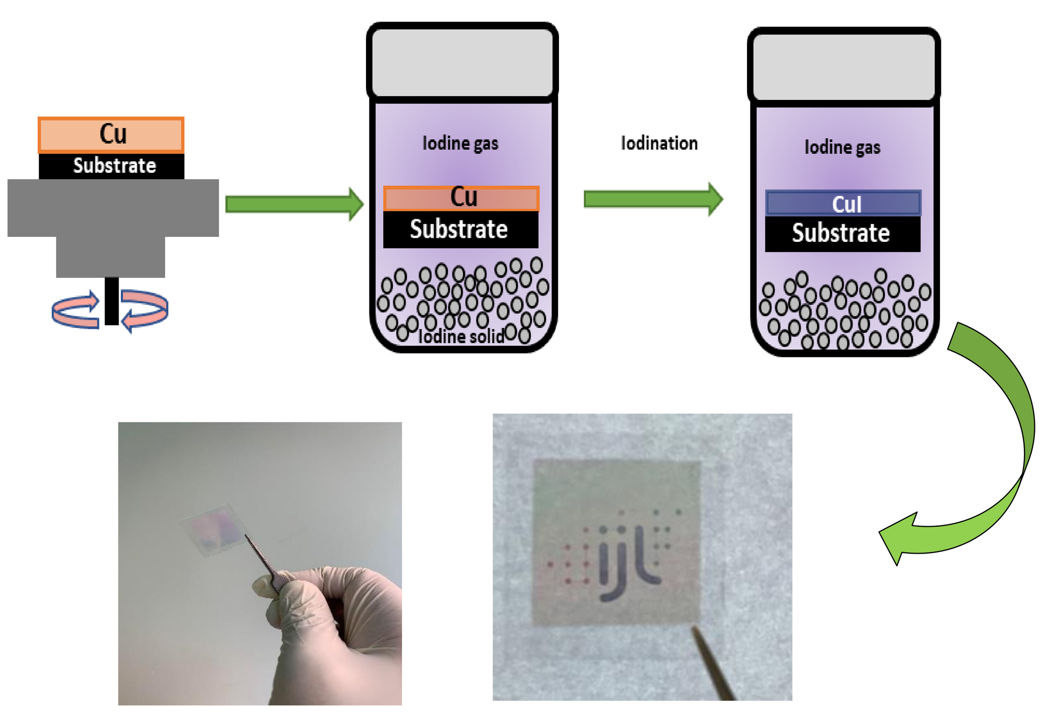
Crystal structures of α, β, and γ allotropes of CuI:



Electrical and optical properties: Application domains

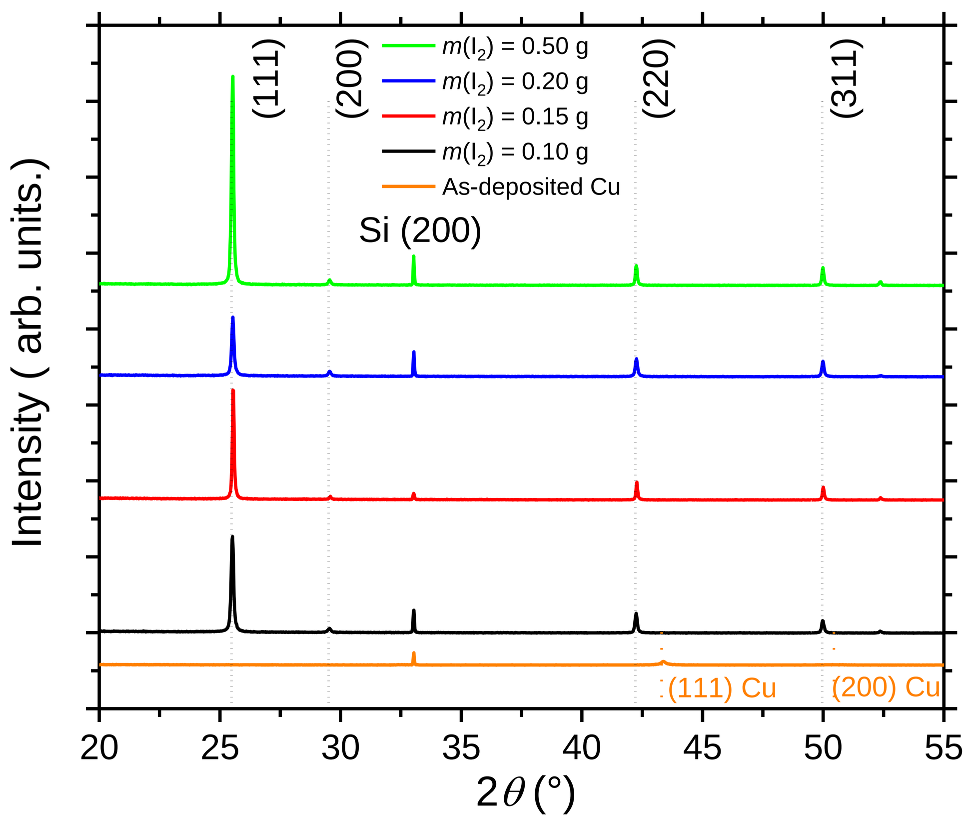
Experimental procedure





Ar flow rate (sccm)	30
Ptotal (Pa)	0.5
Substrate	Glass, Silicon

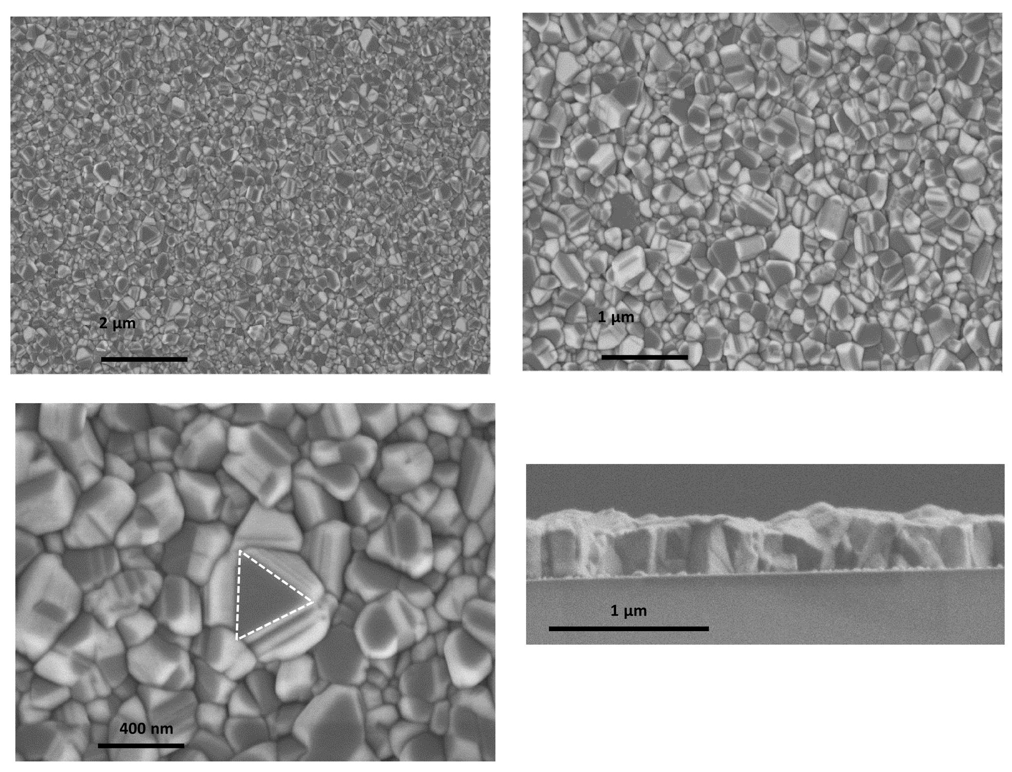
Structure : X-ray diffraction



- Growth of CuI thin films with different amount of Iodine.
- The full width at half maximum (FWHM) of the (111) diffraction peak corresponds to a mean grain size of approx. 60 ± 7 nm.
- The increase of the I_2 mass does not induce a change of the film preferred orientation.
- The allotropic γ− CuI diffraction peaks are coherently indexed in the face centred cubic system and consistent with the **F$\bar{4}$3m** space group.
- The lattice parameter, deduced from the different X-ray diffraction peaks, is a_{γ}−CuI = 0.6054 nm.

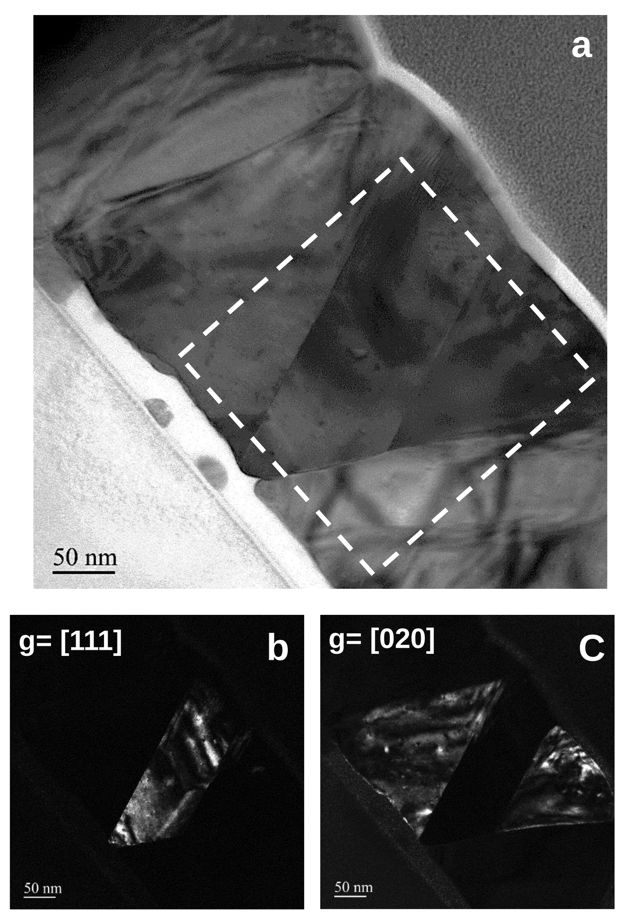
Microstructure

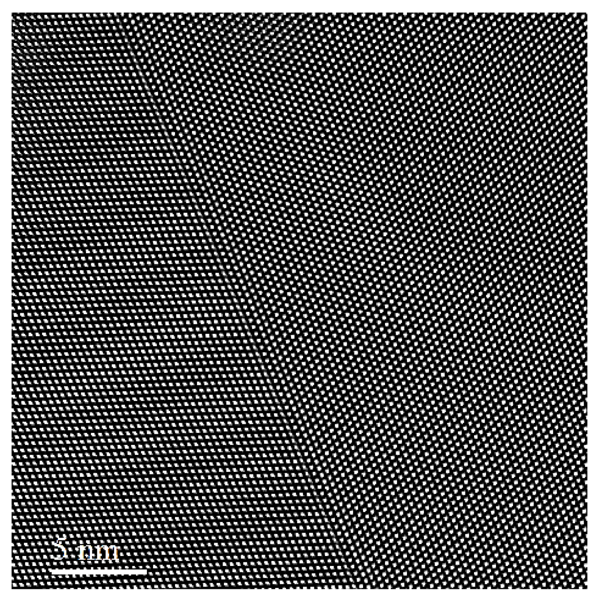
SEM



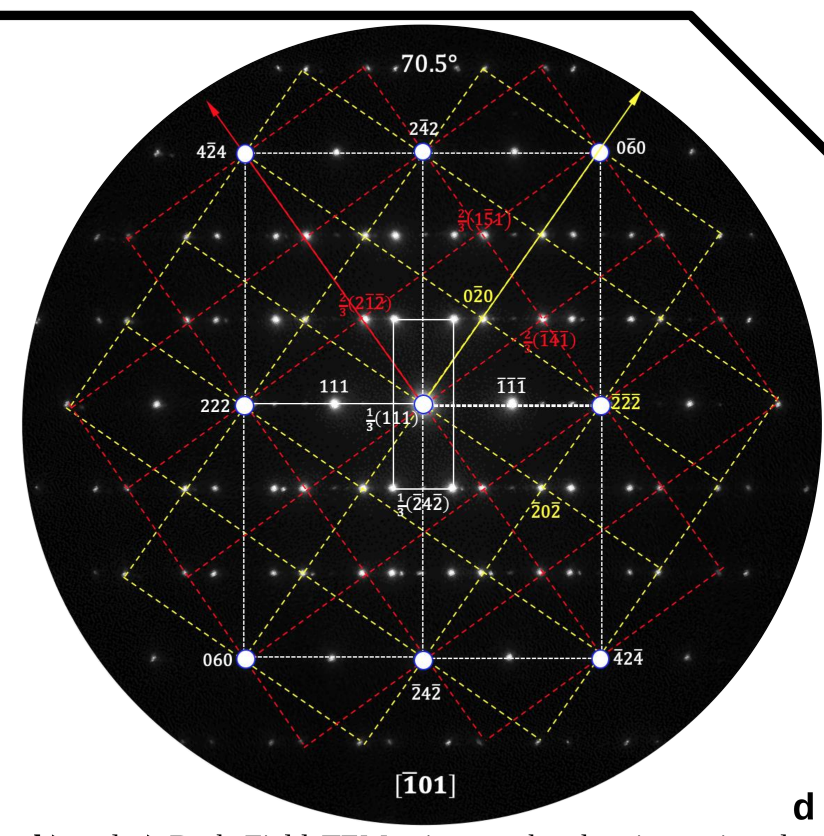
- Top-view SEM images of CuI thin films prepared by 0.15 g of I_2.
- Film thickness is about 300nm
- No porosities observed on the surface.
- Different growth orientations
- Iodination time : 60 minutes.

TEM





STEM micrographs exhibiting the twin plane separating the related twin variants.

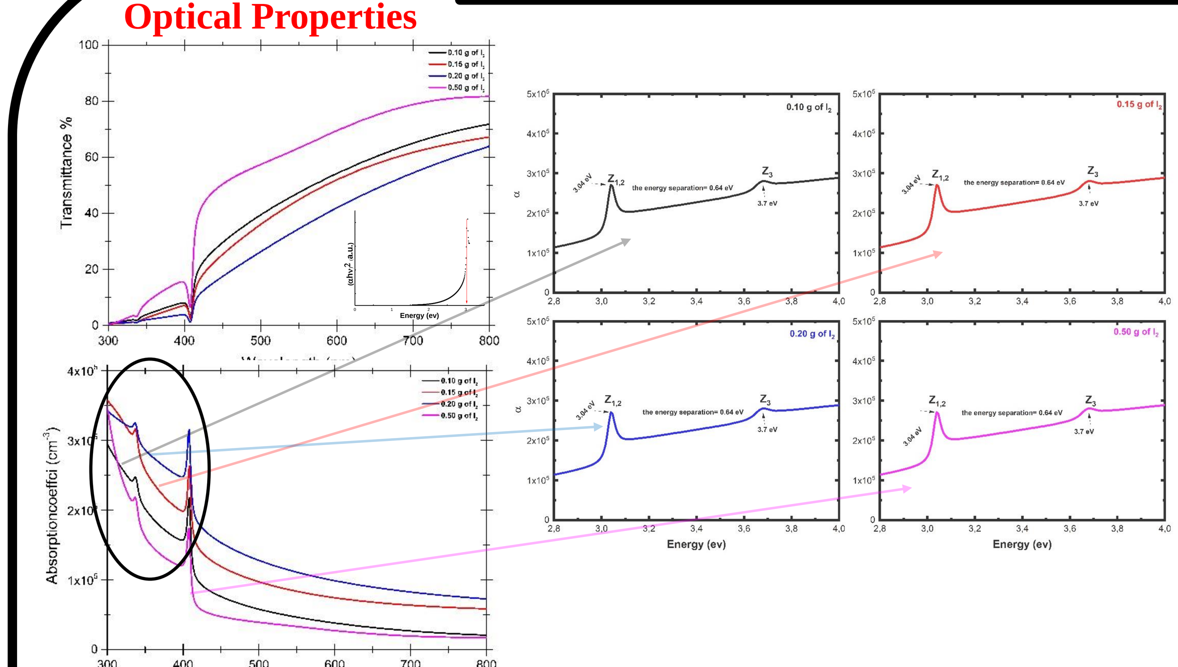


a) Bright, **b)** and **c)** Dark Field TEM micrographs showing twin related variants; **d)** the corresponding composite (red and yellow lattices) diffraction patterns recorded along the common [$\bar{1}$10] zone axis.

The white lattices correspond to the CSL (Coincidence Site Lattice) and DSC (Displacement Shift Complete).

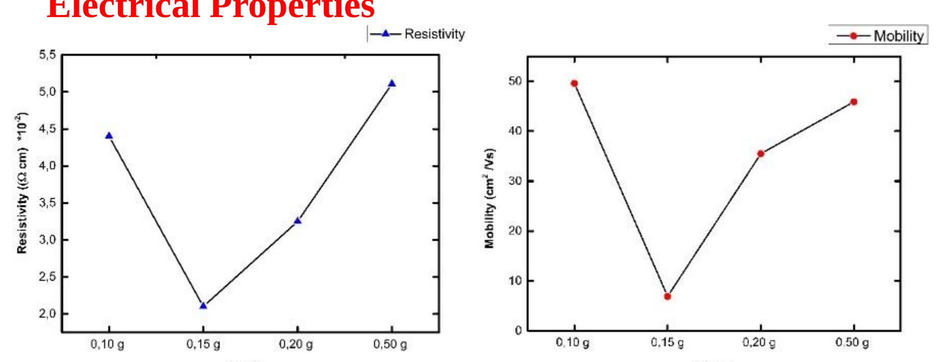
Optical and electrical properties

Optical Properties



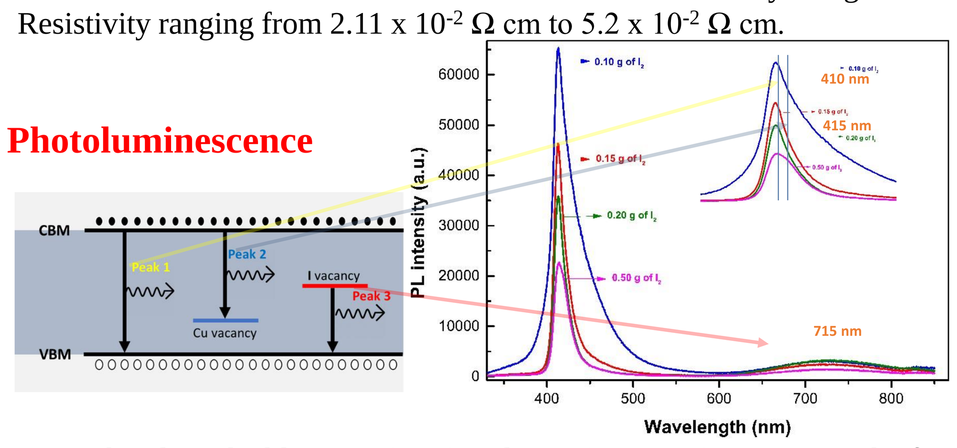
- The direct optical band gap is calculated by Tauc plot: $h\nu\alpha = B(h\nu - E_g)^{1/2}$ When α is absorption coefficient $\alpha = \frac{1}{t} ln \frac{1}{T_{film}}$
- CuI thin films tend to exhibit extremely transmittance and considerable absorption that is over 3 eV as shown by The UV–visible optical transmission measurements (in the wavelength range 400–800 nm).
- The top two doublet at 3.04 and 3.70 eV represent the $Z_{1,2}$ and Z_3 exciton energies.

Electrical Properties



- The electrical measurements of CuI films were carried out by using Hall effect
- Resistivity ranging from 2.11 x 10^{-2} Ω cm to 5.2 x 10^{-2} Ω cm.

Photoluminescence



- Two PL bands in the blue (~400 nm) and NIR (~715 nm) regions can be found
- The assignments of two bands can be referred to band and band to defect state transitions, as depicted in the schematic.
- The fine structure of the PL bands around 400 nm, positions and width, indicates a correlation with the amount of I2 presents inside the material. This likely infers a modification in the electronic structure despite they show the same crystallite size as obtained by XRD.

Conclusion

- CuI have been prepared to investigate its structure, microstructure and properties.
- CuI at different weight of iodine have been prepared to investigate its thin films properties and photovoltaic performance.
- The structural, electrical, and optical properties of CuI thin films deposited on glass and silicon substrates were studied by XRD, Hall effect, UV-VIS spectrometry and photoluminescence. As-prepared film shown [111] preferred orientation, resistivity is ranging from 2.1 and 5.1 × 10^{-2} Ω.cm, hole density (p) is ranging between 1.4 × 10^{18} and 4.3 × 10^{19} cm^{-3}, and mobility μ is ranging between 6.9 and 49.6 $cm^2 . V^{-1}. S^{-1}$
- Transparent p-type semiconductors films and γ-phase of copper iodide (γ-CuI) with wide band gap, Eg ≈ 3.1 eV were obtained.
- Specular transmittance of 40-66% was set at in averaged visible range.
- Thin film morphology, examined by SEM, shows a variation of crystal size and randomly oriented of grains.
- Crystallographic in CuI has been observed by using transmission electron microscopy (TEM).

References

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