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Supplementary Information

Chemical States and Local Structure in Cu-Deficient $Cu_xInSe_{\sim 2}$ Thin Films: Insights into Engineering and Bandgap Narrowing

Ahmed Yousef Mohamed [a,b,*], Byoung Gun Han [a], Hyunseo Jang [a], Jun Oh Jeon [a], Yejin Kim [a], Haeseong Jang [c], Min Gyu Kim [d], Kug-Seung Lee [d], Deok-Yong Cho [a,*]

[a] Department of Physics, Jeonbuk National University, Jeonju 54896, Republic of Korea.

[b] Department of Physics, Faculty of Science, South Valley University, Qena 83523, Egypt.

[c] Department of Advanced Materials Engineering, Chung-Ang University, Anseong 17546, Republic of Korea.

[d] Pohang Accelerator Laboratory, Pohang 37673, Republic of Korea

1. Interatomic Diffusion in Cu_xInSe_2 Fabrication Process

The diffusion dynamics at a given temperature T can be quantified by diffusion coefficient D in Arrhenius equation of $D=D_0 \exp(-Q/RT)$, where D_0 is a pre-exponent factor, Q is the activation energy, and R is the gas constant [1].

Cu_xInSe_2 samples were prepared by (Process 1) growth of In/Cu multilayer using e-beam evaporation and (Process 2) heating the multilayer sample to 500 °C under Se vapor ambiance. During Process 2, In melts and is mixed with Cu, and at the same time, Se vapor permeates into the Cu+In films to be ionized. Therefore, the two diffusion processes are considered; (A) Diffusion of In into Cu and (B) diffusion of Se vapor into CuIn alloy.

(A) In diffusion into Cu: According to the literature [1,2], the D value at T = 300 °C of In into Cu is calculated to be ~2.3×10^{-12} m^2/s.

(B) Se vapor diffusion into CuIn: According to the literature [3], the D value at T = 300 °C of Se into CuInGaSe or $CuInSe_2$ was estimated to be ~6.7×10^{-16} m^2/s.

From Fick's second law of diffusion, the order of the time scale for homogeneous diffusion for a given diffusion length L and diffusion coefficient D, is given as ~$L^2/4D$ [4]. Since the TEM-EDX results show a complete diffusion of In and Se, it is reasonable to set L approximately to be the film thickness ~50 nm. The calculated time scales for complete diffusion are in the order of (A) milliseconds or (B) seconds, definitely less than a minute for both (A) and (B). In Process 2, the heat was applied at T = 500 °C at least for 5 min. Thus, it can be concluded that the time was enough for the interatomic diffusion to form a uniform $CuInSe_2$ phase.

2. Calculation of the [Cu]/[In] Ratios

The atomic ratios of the elements in the $Cu_xInSe_{\sim 2}$ thin films were determined using EDX analysis and are shown in Table S1. Accordingly, the [Cu]/[In] ratios from EDX analysis are 0.34, 0.46, 0.78, and 0.99 for CISe-1, CISe-2, CISe-3, and CISe-4, respectively.

Table S1. The atomic ratios of the elements in the $Cu_xInSe_{\sim 2}$ thin films using EDX analysis, where x = [Cu]/[In].

Samples	Cu At%	In At%	Se At%	Total	[Cu]/[In]	[In]/[Se]	[Cu+In]/[Se]
CISe-1	11.86	34.91	53.24	100.00	0.34	0.66	0.88
CISe-2	14.15	30.96	54.90	100.00	0.46	0.56	0.82
CISe-3	20.98	27.07	51.95	100.00	0.78	0.52	0.92
CISe-4	24.61	24.96	50.43	100.00	0.99	0.50	0.98

3. FE-SEM

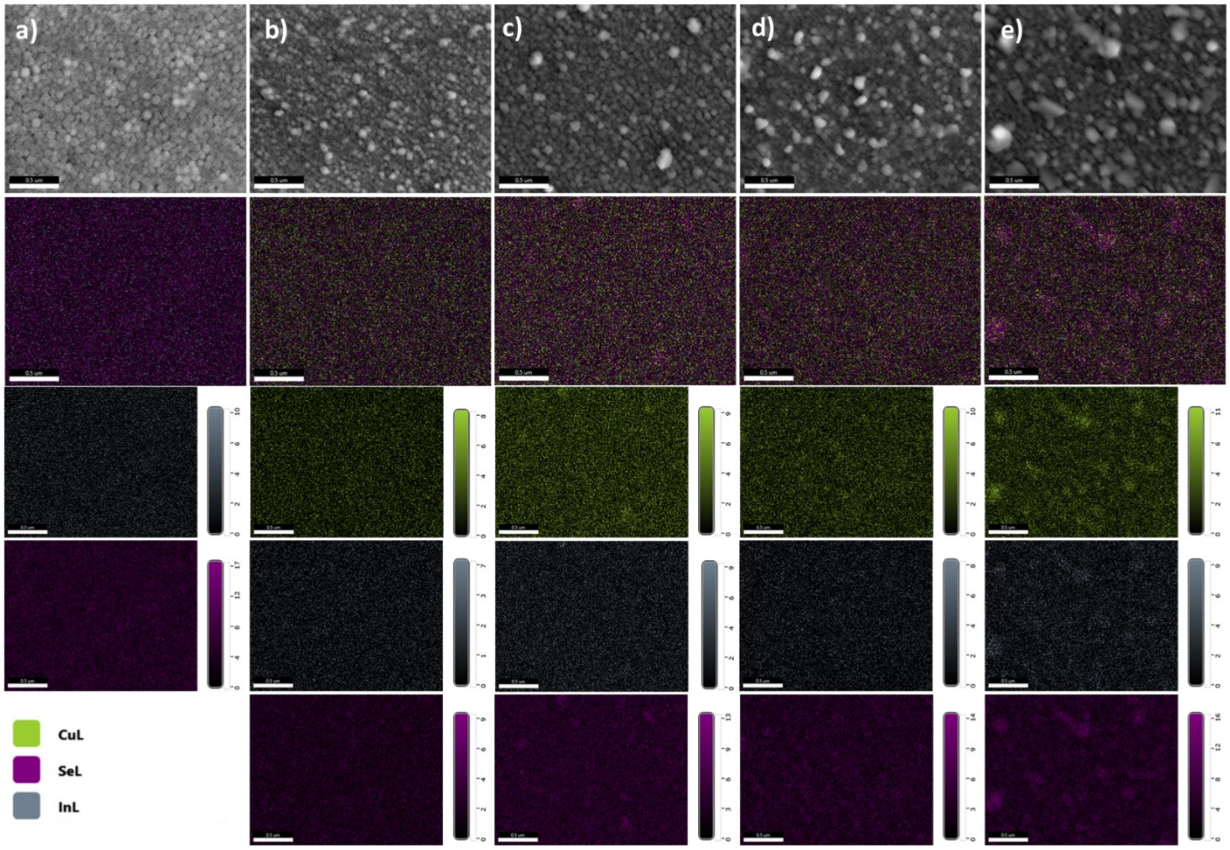

Figure S1. FE-SEM images with EDS mapping show the atom distribution mapping on the samples' surfaces, a) the In_2Se_3 reference sample and b)-e) the $Cu_xInSe_{\sim2}$ thin films at [Cu]/[In] ratios of 0.34, 0.46, 0.78, and 0.99, respectively. These results show that the Cu, In, and Se atoms are distributed uniformly on the surface of the thin film.

4. Cs-TEM

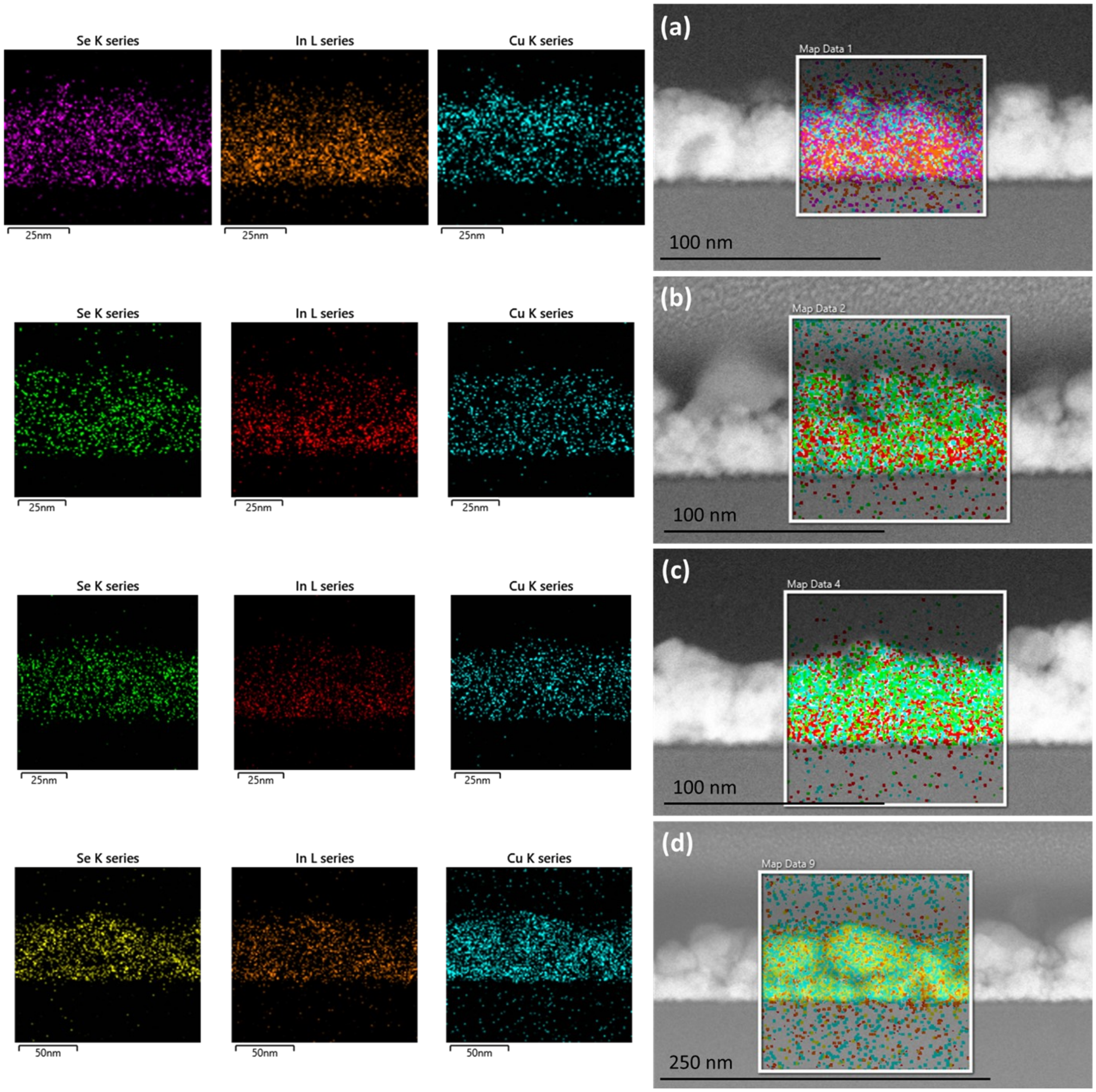

Figure S2. Cross-sectional TEM images and the EDX mapping taken across the film/Si interfaces in the $Cu_xInSe_{\sim 2}$ thin films at [Cu]/[In] ratios of 0.34, 0.46, 0.78, and 0.99. These results show that the Cu, In, and Se atoms are distributed uniformly throughout the thickness of the thin films. The thickness of the samples has been determined to be in the range of approximately 30 to 60 nm.

5. XPS Survey Scans

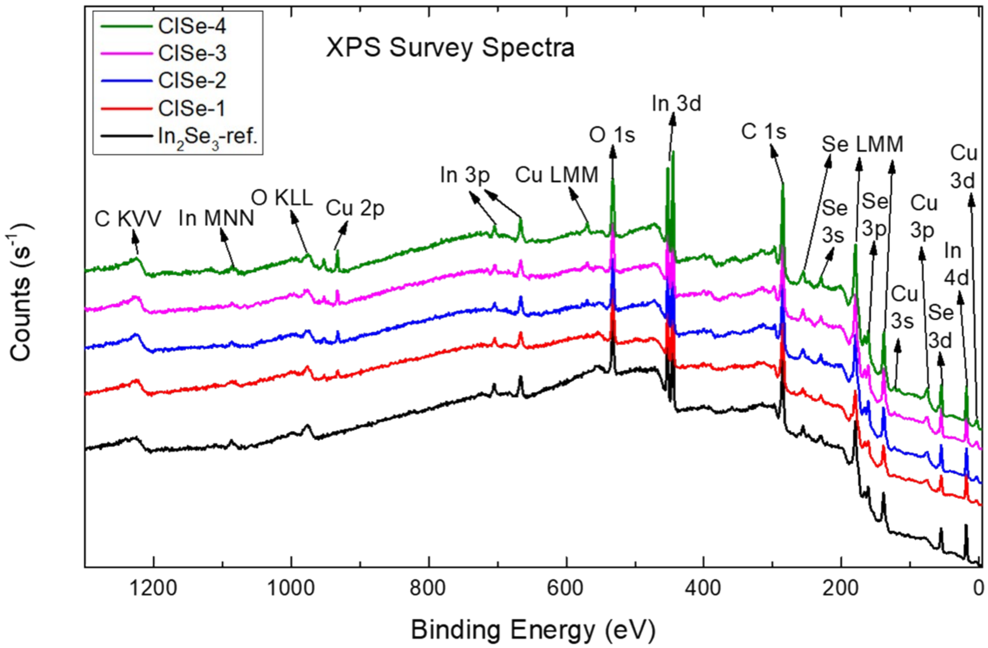

Figure S3. XPS survey scans of the In_2Se_3 reference sample and $Cu_xInSe_{\sim 2}$ thin films at [Cu]/[In] ratios of 0.34, 0.46, 0.78, and 0.99. This shows the presence of Cu, In, Se, O, and C in the samples. It was observed that all elements were found in their expected oxidation states; however, the O was observed due to the presence of surface contamination. All XPS spectra were calibrated by the C 1s peak (284.6 eV).

6. XAS: Cu K-edge EXAFS analysis

Table S2. The results of EXAFS analyses for the Cu-Se shells in $Cu_xInSe_{\sim2}$. N is the coordination number, R+*ΔR* is the scattering-phase-corrected interatomic distance, and σ^2 is the disorder factor.

Sample	Scattering Path	*N*	*R+ΔR* in Å	σ^2 in Å^2
CISe-1	Cu-Se	3.9 (± 0.2)	2.421 (±0.005)	0.007 (±0.001)
CISe-2	Cu-Se	3.9 (± 0.2)	2.410 (±0.005)	0.007 (±0.001)
CISe-3	Cu-Se	3.9 (± 0.2)	2.407 (±0.005)	0.007 (±0.001)
CISe-4	Cu-Se	3.9 (± 0.2)	2.407 (±0.004)	0.007 (±0.001)

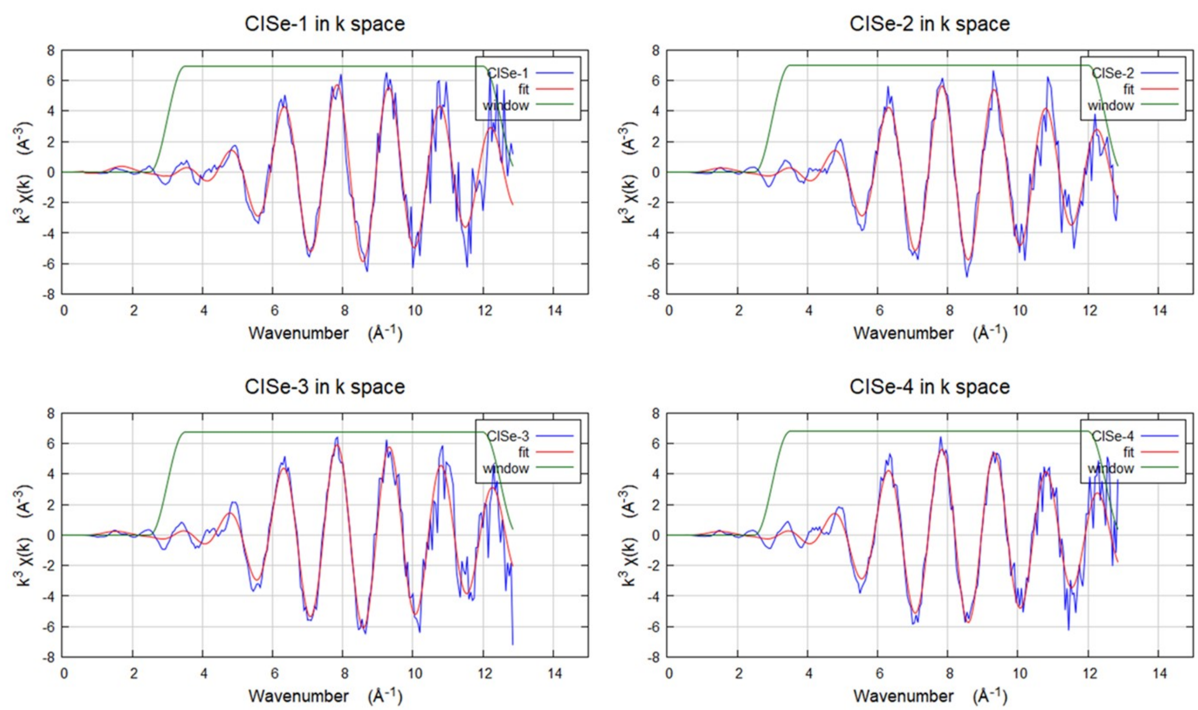

Figure S4. The fitting results of Cu K-edge EXAFS analyses in k-space for the Cu-Se shells in $Cu_xInSe_{\sim2}$.

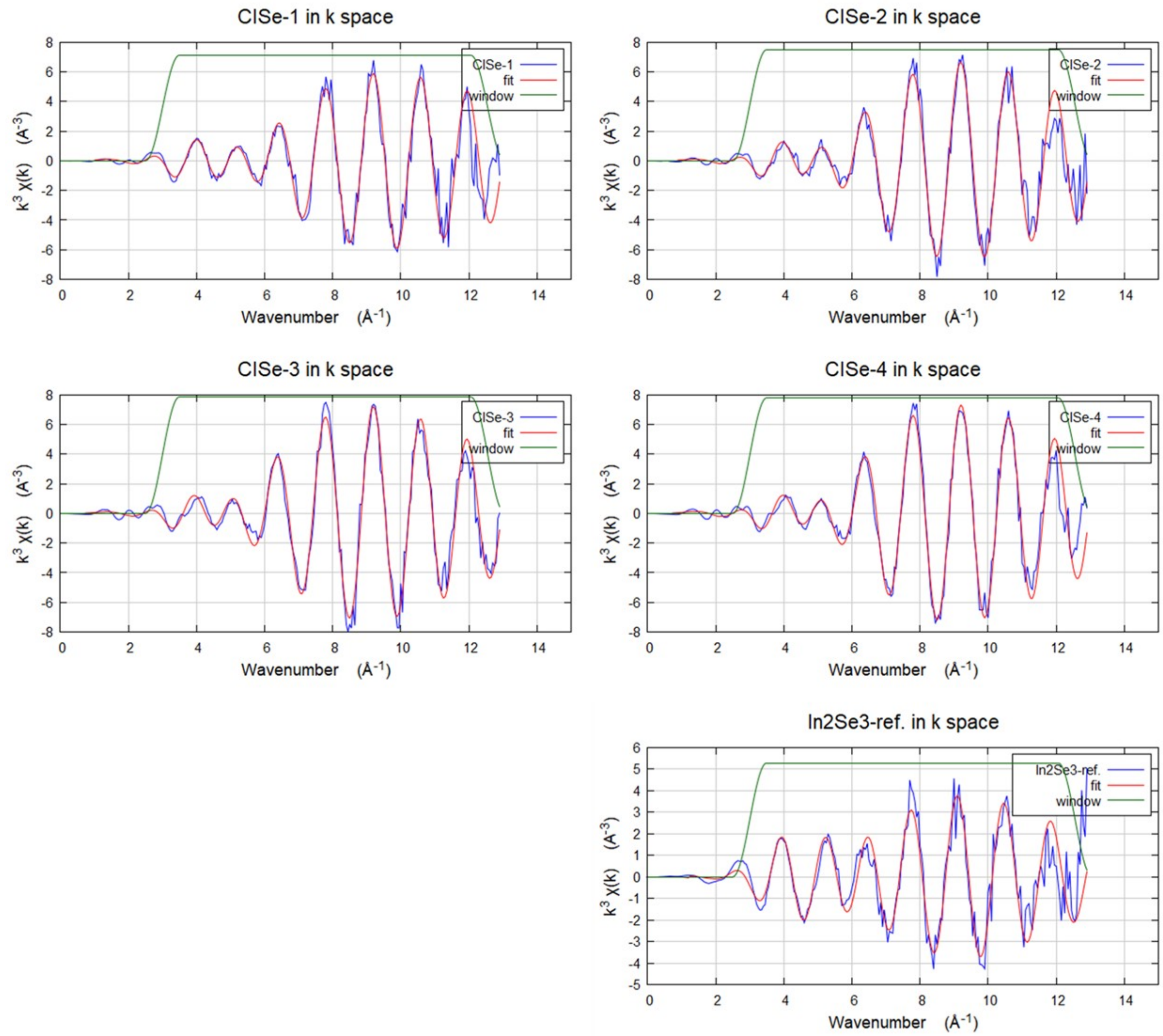

Figure S5. The fitting results of Se K-edge EXAFS analyses in k-space for the Se-Cu and Se-In shells in $Cu_xInSe_{\sim 2}$.

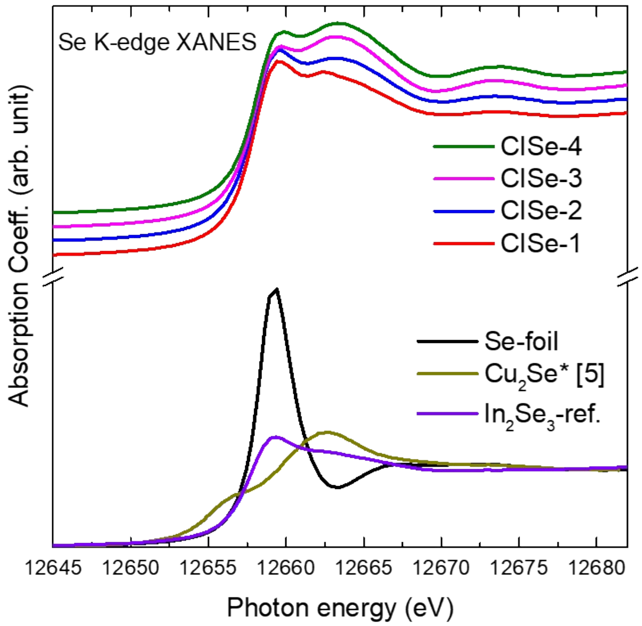

Figure S6. Se K-edge XANES of the $Cu_xInSe_{\sim 2}$ samples in comparison with In_2Se_3 reference sample and reported Cu_2Se reference [5].

References

(1) Gale, W. F.; Totemeir, T.C. (Eds.), *Smithells Metals Reference Book* 8th edition (Elsevier 2004), Chapter 13.

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(3) Wang, J.; Zhang, Y.; Zhu, J. Diffusion Coefficients of Selenium and Gallium During the $Cu(In_{1-x}Ga_x)Se_2$ Thin Films Preparation Process, *Advanced Materials Research* **2013**, 815, 448-453.

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