

Supplementary information

**Formation of wide-bandgap, highly transparent and compact Cd<sub>1-x</sub>Zn<sub>x</sub>S films  
with dynamically controlled pH in chemical bath deposition**

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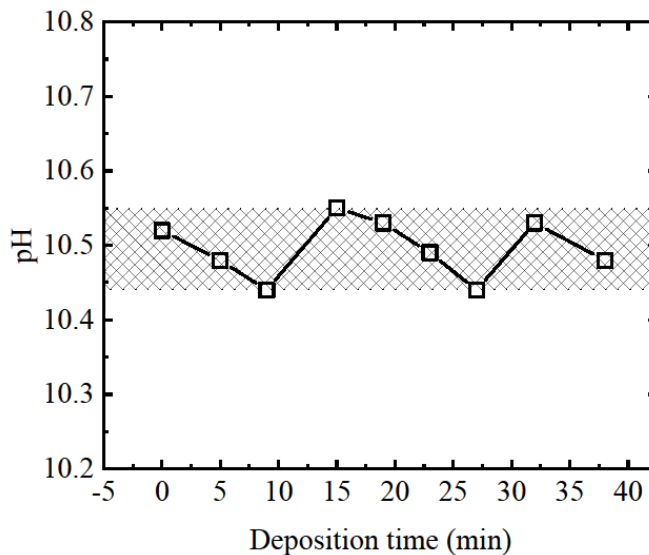
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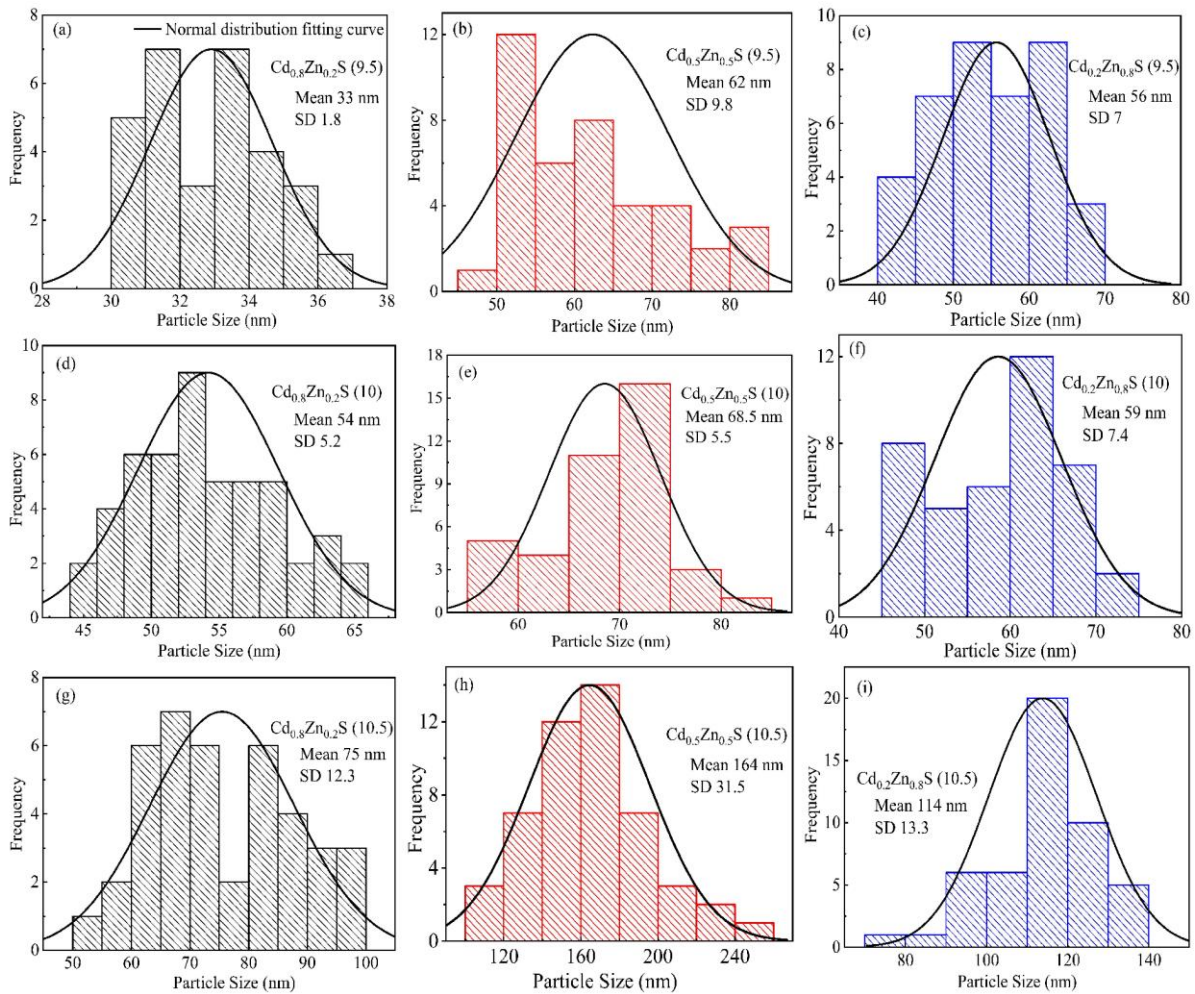
### Supplementary note 1:



**Fig. S1** Typical representation of the dynamic maintenance of solution's pH throughout the deposition time in the chemical bath at  $\sim 10.5$ .

As ammonia is volatile, maintaining pH during the deposition is crucial to assess the accurate response of pH on film formation and its properties. **Fig. S1** illustrates the representative curve of dynamic maintenance of the pH of the chemical bath at  $\sim 10.5$ . The highest and lowest pH of the solution is 10.55 and 10.44, respectively. The pH of the solution is thoroughly monitored using the pH meter, and ammonia solution is used to maintain the narrow range of the pH level. Samples are also prepared at two other pH:  $9.5 \pm 0.06$  and  $10 \pm 0.06$ .

## Supplementary note 2:



**Fig. S2** Particle size distribution with average particle size and standard deviation of all samples prepared at different pH of the bath- (a-c) 9.5, (d-f) 10 and (g-i) 10.5.

**Fig. S2** depicts the particle size distribution of the prepared samples. The average particle size increases for all three Zn compositions ( $x = 0.2, 0.5$  and  $0.8$ ). A slight variation of the average particle size (from 56 nm to 75 nm) is observed in case of fully covering, compact films (c, e and g). On the other hand, films having poor coverage (h and i) show relatively larger average particle sizes ( $> 100$  nm).

**Supplementary note 3:**

Table S1: The obtained EDS result of the prepared samples from 10 different points.

Sample	pH	Zn (atom %)	Cd (atom %)	S (atom %)
Cd <sub>0.8</sub> Zn <sub>0.2</sub> S	9.5	13.35± 2.23	42.77± 1.02	43.88± 1.39
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S		20.18± 1.1	50.42± 1.26	29.40± 1.36
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S		20.92± 1.06	45.61± 0.98	33.47± 0.88
Cd <sub>0.8</sub> Zn <sub>0.2</sub> S	10	16.37± 1.44	52.088± 1.31	31.55± 1.29
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S		13.31± 1.48	51.7± 1.37	35± 1.53
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S		29.35± 2.36	39.65± 3.38	30.07± 2.65
Cd <sub>0.8</sub> Zn <sub>0.2</sub> S	10.5	4.54± 0.84	56.11± 1.31	39.35± 1.08
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S		11.87± 0.69	45.73± 1.2	42.4± 1.38
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S		36.25± 1.68	35.35± 1.27	28.4± 2.35

Table S2: The obtained EDS result of the prepared optimum samples from 30 different points.

Sample	pH	Zn (atom %)	Cd (atom %)	S (atom %)
Cd <sub>0.8</sub> Zn <sub>0.2</sub> S	10.5	4.77± 0.61	54.54± 0.82	40.69± 0.80
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S	10	13.34± 1	50.92± 1.09	35.73± 0.96
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S	9.5	19.21± 0.75	46.19± 0.82	34.60± 0.94

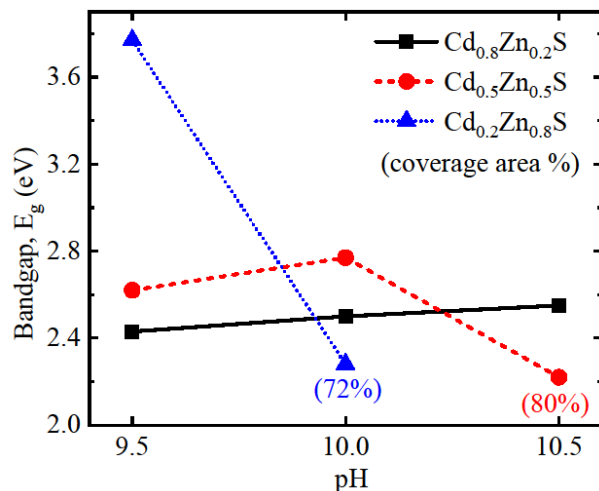
### Supplementary note 4:

The interaction volume is found to directly proportional to the penetration depth. Penetration depth depends on the material and accelerating voltage used. It can be estimated as following [1]:

$$H = \frac{0.0276 A V^{1.67}}{Z^{0.89} \rho} \mu\text{m}$$

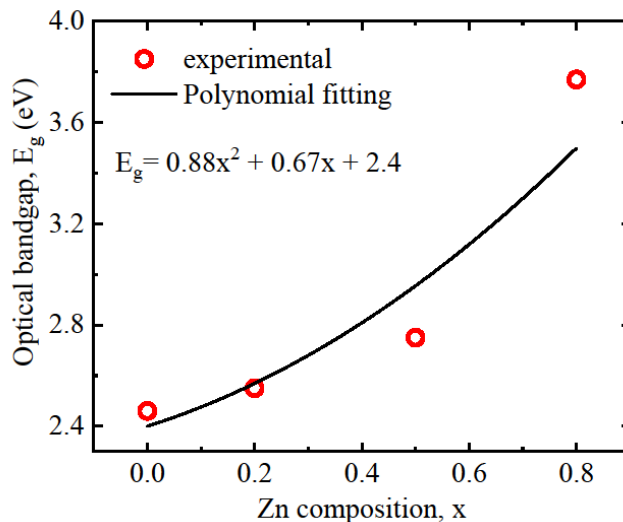
Where, H= penetration depth ( $\mu\text{m}$ ), A= weight ( $\text{g mol}^{-1}$ ), V= accelerating voltage (kV), z= atomic number and  $\rho$ = density ( $\text{g cm}^{-3}$ ).

Considering the film consisting solely of Cd and Zn, the penetration depth is found to be ~350 nm and ~400 nm, respectively. While calculating the penetration depth of CdS and ZnS (using the atomic number of Cd and Zn accordingly), it becomes ~600 nm and ~670 nm, respectively. Given the deposited films' thickness, the interaction between the striking electrons and the substrate is inevitable. Therefore, peaks of elements other than Cd, Zn and S are found in the EDS spectra.

**Supplementary note 5:**

**Fig. S3** The optical bandgap ( $E_g$ ) of  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  and  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  films prepared at different pH.

$E_g$  of all the fabricated samples except  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  film deposited at pH- 10.5 is depicted in **Fig. S3**. In  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  films,  $E_g$  gradually increases with the increasing pH of the bath. With increasing pH, the film formation mechanism changes from the homogeneous to the heterogeneous mechanism, resulting in improved morphology. Similar improvement of morphology increases  $E_g$  of  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  films. However, owing to the poor coverage, inconsistency in  $E_g$  is observed for  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  film deposited at pH- 10.5. Similarly, the anomaly of  $E_g$  is found in  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  film deposited at pH- 10 for incomplete coverage.

**Supplementary note 6:**

**Fig. S4** Quadratic fit of the extracted bandgap data as a function of Zn mole fraction

The bandgap of some alloy systems follows Vegard's law and can be determined from a linear interpolation of the bandgap values as a function of constituent elements. However, the relative size of constituent elements, inhomogeneity and several other factors cause the deviation from Vegard's law. The deviation is represented by the bowing parameter determined by fitting the experimental values with a quadratic expression. The coefficient of  $x^2$  is called the bowing parameter and is characteristic of a particular alloy system. It appears from [Fig. S4](#) that  $E_g$  varies slowly with  $x$  for Cd-rich compositions while increasing rapidly for the Zn-rich end. A similar non-linear variation of optical band gap was also reported for solution grown  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  alloys [2].

## References

- [1] K. A. Kanaya, S. Okayama, Penetration and energy-loss theory of electrons in solid targets, *J. Phys. D* 5.1 (1972) 43–58. <https://doi:10.1088/0022-3727/5/1/308>.
- [2] S. Borse, S. Chavhan, R. Sharma, Growth, structural and optical properties of cd1- xznxs alloy thin films grown by solution growth technique (sgt), *Journal of Alloys and Compounds* 436 (2007) 407–414. <https://doi.org/10.1016/j.jallcom.2006.11.009>