Supplementary Information

Title: "Investigation of CsPbBr$_3$ CVD dynamic at different temperatures"

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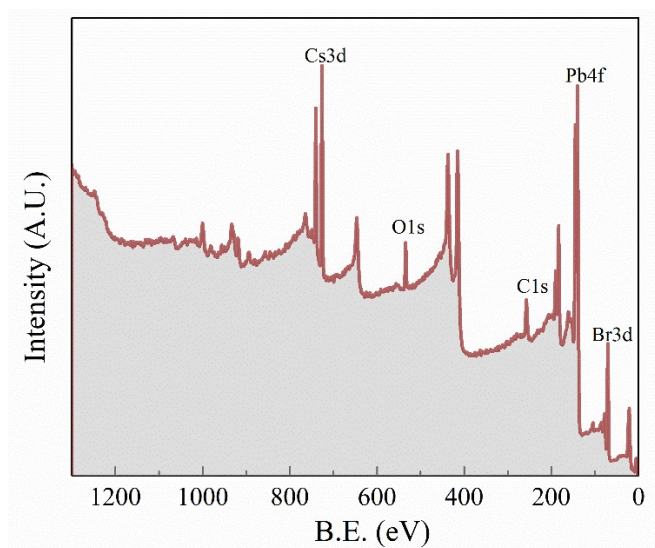***Corresponding emails:** longhao@xmu.edu.cn

1. XPS results:

Fig.S1: XPS of CsPbBr$_3$ deposited at 250°C.

Element	B.E.(eV)	Area	Measured Atomic Percentage	Excepted Atomic Percentage
Cs	725.28	69582	18.33	20.00
Pb	139.19	73075	24.07	20.00
Br	69.00	14421	57.60	60.00

Table S1: Analyzation of XPS data.

2. Crystalline size, dislocation density and strain of perovskite by XRD

According to the literature[1-3], 2θ angle and width of powder XRD curves β were analyzed to investigate the average crystalline size D, dislocation density ρ and strain ε. Average crystalline size D was calculated by Debye Scherrer's Equation:

$$D = \frac{0.9\lambda}{\beta \cos(\theta)} \quad (1)$$

where λ is the X-ray wavelength ($0.154\ nm$).

Dislocation density and strain were calculated by:

$$\rho = 1/D^2 \quad (2)$$

$$\varepsilon = \beta/4\tan\theta \quad (3).$$

Results were shown in Table S2:

Table S2：Parameter calculated from XRD curves

Temperature（ºC）	D(nm)	$\rho(\mu m^{-1})$	ε (%)		Notes
30	63.2	250.3	0.29		
100	70.4	202.0	0.26		
150	48.4	426.1	0.38		
200	82.1	148.2	0.22	✓	Best quality
				✓	Decent deposition rate
250	50.9	385.1	0.35		Highest deposition rate
300	46.4	462.5	0.39		

From Table S2 and Fig.4, the perovskite thin film deposited at 200 ºC appeared lowest dislocation density and decent deposition rate.

3. Reactant concentration in chamber:

To calculate the reactant concentration in chamber (n^c), we assumed that the solid CsBr and PbBr$_2$ powders were firstly melted (actually we indeed observed the melted and recrystallized CsBr and PbBr$_2$ in reactant crucible after CVD growth). There is an equilibrium between gas/liquid phase at the interface between melted powder and chamber gas. The gas/solid phase equilibrium line (P-T) could be expressed:

$$ln\,P_c/P_1 = \frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_c}\right) \quad (4);$$

where $\Delta_{vap}H_m$, R were the molar vaporization enthalpy and molar gas constant; P_c, T_c were saturated vapor pressure and temperature in chamber. (P_1, T_1) were any known vaporization point on phase equilibrium line. According to Langes Chemistry Handbook[4], when P_1 is one bar, the vaporization temperature T_1 of CsBr and PbBr$_2$ are 1300ºC and 914ºC,

respectively. As $T_c = 500°C$ was set to heat reactant powders in first furnance, the saturated vapor pressure P_c could be derived as: $P_c = 118$ Torr of CsBr and 243Torr of $PbBr_2$.

With the saturated vapor pressure P_c, the reactant concentration in chamber ($n^c = N/V$) could be calculated by:

$$n^c = N/V = P_c/RT \tag{5}.$$

In our calculation, $n_{CsBr}^c = 2.4\ mol/m^3$ and $n_{PbBr_2}^c = 5.05\ mol/m^3$ were derived.

4. *Diffusion coefficient (D):*

The diffusion coefficient represented the capability of single molecular diffusing to target:

$$D = \frac{1}{3}\bar{v}l \tag{6}$$

where $\bar{v}$, l were mean velocity and diffusion length of reactant. In this study, the mean velocity was estimated by thermal motion:

$$\bar{v} = \sqrt{\frac{3k_B T}{m}} \tag{7}.$$

The mean diffusion length was estimated by:

$$l \approx \frac{1}{n^c d^2} \tag{8},$$

where d is the diameter of reactant molecules. Therefore, the diffusion coefficients D were calculated to be: 3.95 cm^2/s of CsBr and 0.4 cm^2/s of $PbBr_2$. It shows that the diffusion ability of $PbBr_2$ was pretty weaker than CsBr.

5. *Diffusion layer thickness δ*

The conception of diffusion layer thickness comes from laminar flow of fluid mechanics.
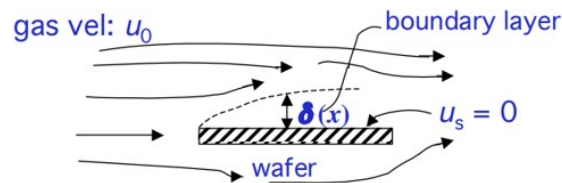

Fig.S2: diagram of gas flow through substrate surface.

As shown in Fig.S2, when reactant gas flow through substrate, a boundary layer formed on the wafer surface with no velocity. Reactant diffuses through this boundary layer into substrate. The average diffusion layer thickness could be calculated by:

$$\delta = \frac{1}{L}\int_0^L \sqrt{\frac{\eta x}{\rho u_0}}dx = \frac{2}{3}L\sqrt{\frac{\eta}{\rho u_0 L}}$$

(9);

where L is the substrate length of 2cm; η was the coefficient of viscosity; ρ was the density; u_0 was the gas velocity, which was estimated to be 0.38m/s by vacuum pump's pumping speed (3L/s). η was calculated based on Sutherland's theorem:

$$\eta = \eta_0\left(\frac{T}{T_c}\right)^{1.5}\frac{T_c + T_s}{T + T_s}$$

(10)

As we know $\eta_0 = 16.6\times10^{-6}$, $T_c = 273K$ and $T_s = 104K$ of nitrogen (N_2) carrier, the η could be derived at different substrate temperature T.

With all above n^c, δ and D ready, the inflow of reactants could then be readily calculated:

$$I = \frac{D}{\delta}\cdot(n^c - n^{sub})$$

(11)

6. Vibration frequency f(T,m) in desorption coefficient α:

In this work, we utilized Lindemann criterion[5] (molecules desorbed from substrate when their displacement exceeding 1/10 lattice distance) to estimate the frequency $f(T,m)$:

$$f(T,m) = \frac{v}{0.1d} = \frac{\sqrt{2k_BT/m}}{0.1d}$$

(12).

The velocity v was estimated by thermal motion of molecular.

References:

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