Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Development of Moisture-Proof Polydimethylsiloxane/Aluminum Oxide Film and Stability Improvement of Perovskite Solar Cells Using the Film

Eun Young Choi[†, ‡], *Ju-Hee Kim*[†, ‡], *Bu-Jong Kim*[†], *Ji Hun Jang*[†], *Jincheol Kim*[*, †, §] *and Nochang Park*[*, †]

The relationship between WVTR and lag time

To define the meaning of lag time, we firstly introduce some equations related diffusion. The distribution of water vapor concentration at certain barrier thickness can be expressed using the Fick's second law as shown in the below equation.[1]

$$c(x,t) = C1\left(1 - \frac{x}{l}\right) - \frac{2C1}{\pi}\sum_{n=1}^{\infty} - \frac{1}{n}\sin\left(\frac{n\pi x}{l}\right) exp\left(- \frac{Dn^2\pi^2 t}{l^2}\right) \quad (1)$$

If above equation is differentiated by x, we can calculate the flow rate of the vapor. And the total amount of vapor passing through barrier can be expressed by integrating obtained the flow rate as follows:

$$Q(t) = \frac{DtC_1}{l} - \frac{lC_1}{6} - \frac{2lC_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(- \frac{Dn^2\pi^2 t}{l^2}\right) \quad (2)$$

, where D means the diffusion coefficient of barrier layer, C1 means the moisture concentration on the surface of barrier, l is the thickness of barrier film, t is time and Q describes the total amount of water vapor that ingress. If time is becomes infinitely value, the exponential part of equation converges to zero and the equation can be simplified like below.

$$Q(\infty) = \frac{DC_1}{l}\left(t - \frac{l^2}{6D}\right) \quad (3)$$

This equation can be drawn with x axis as time (t) and y axis as quantities of vapor (Q). In this case, the slope of the equation represents flow rate of vapor and intercept of x means the lag time of barrier layer.

In other words, the concentration of moisture vapor penetrating through the barrier increases continuously over time. After a while, the concentration of moisture is in a steady state due to the diffusion of moisture through the barrier. The "lag time" is defined as the time of the steady state and the phenomenon can be seen at the graph of conductance graph. Therefore, we obtained the lag time through the time of steady state at the conductance graph of our Ca samples with various encapsulation method

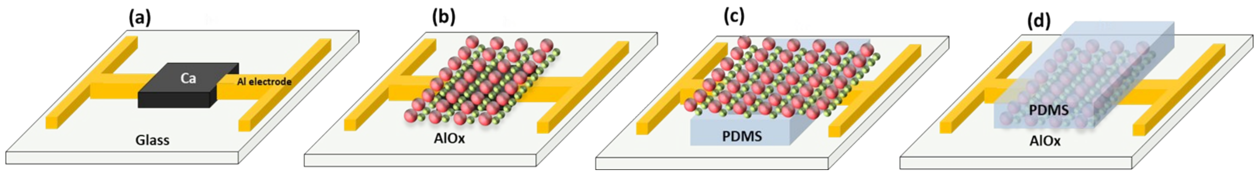

Figure S1. Structure of Ca cell and encapsulation. (a) Ca cell, (b) Ca cell encapsulated by the AlO_x thin film, and (c)–(d) Ca cell encapsulated by PDMS and AlO_x thin film

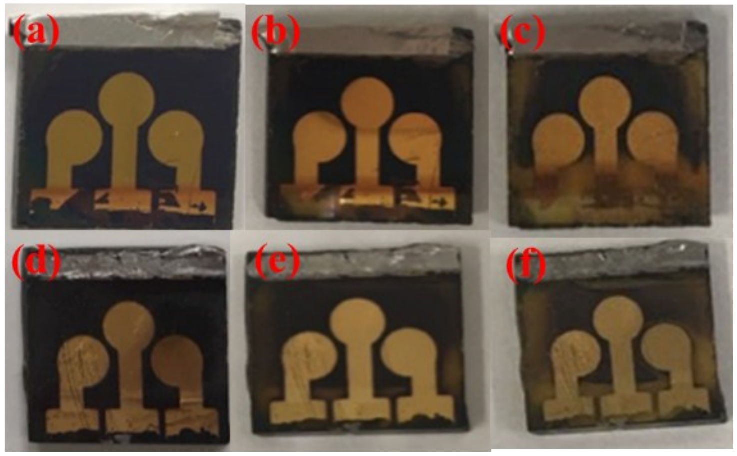

Figure S2. Digital photograph of the perovskite cell with encapsulation, before and after the damp heat test (45 °C and 65 % RH)

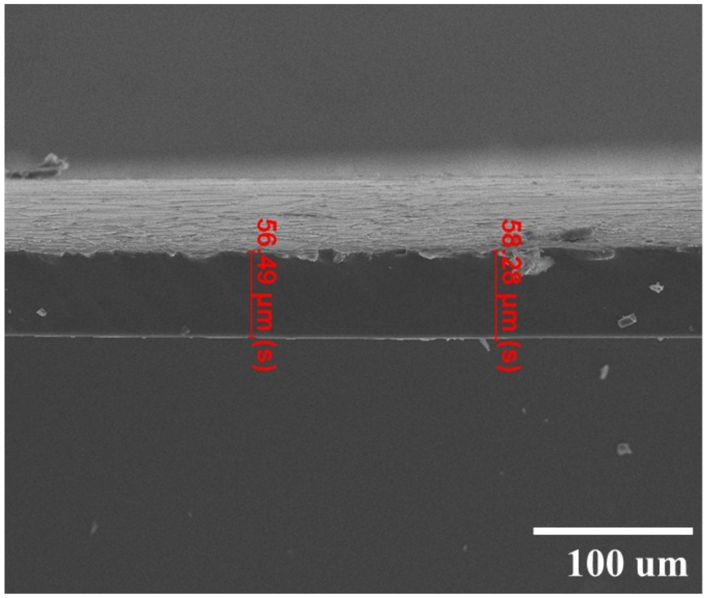

Figure S3. PDMS thickness mesured by Scanning electron transmission (SEM)

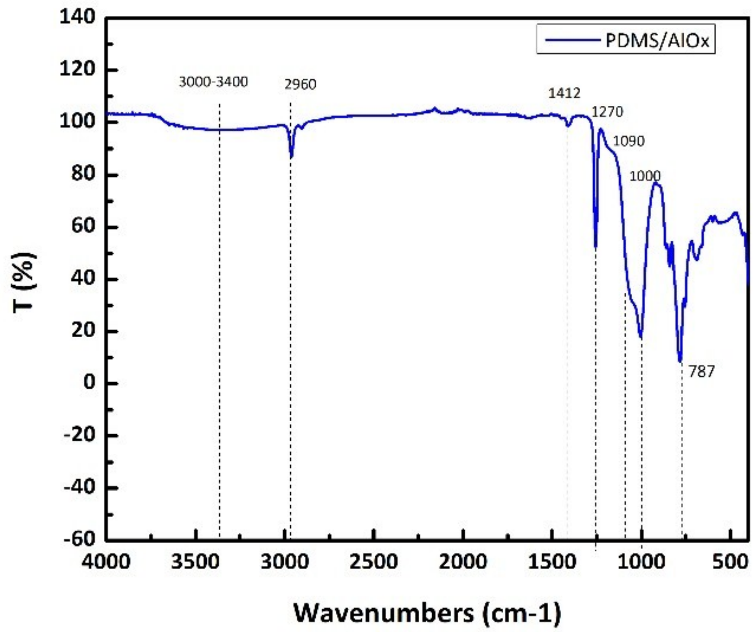

Figure S4. FTIR spectra of PDMS/AlOx barrier

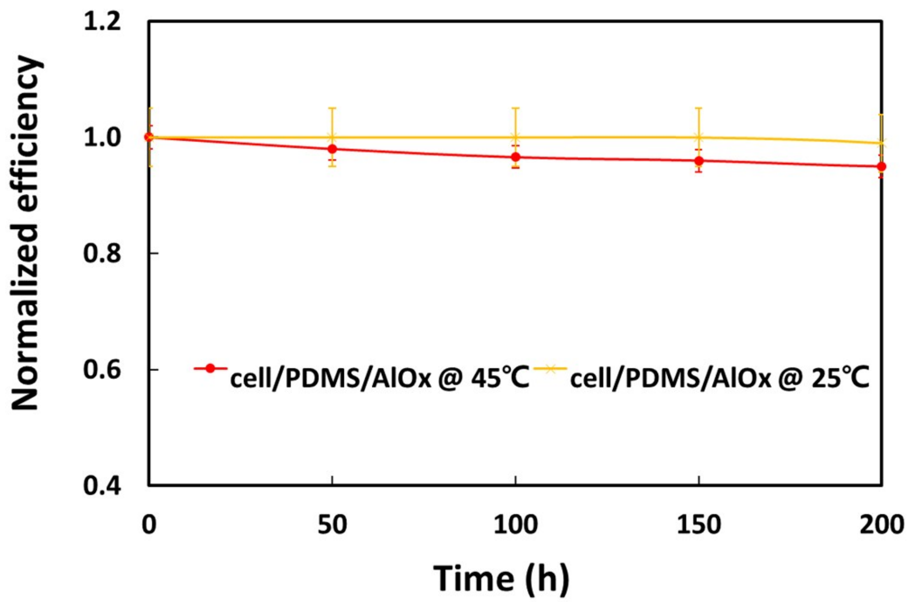

Figure S5. Power conversion efficiency of perovskite photovoltaic cells with AlO_x or PDMS/AlO_x at 25 °C or 45 °C in 65 % RH condition

Table S1. Summarization of reported literatures about encapsulation barrier.

Material	WVTR [g m^{-2} d^{-1}]	Comments Device type, Device structure, stability	Reference in manuscript
CYTOP/ALD Al_2O_3/MgO	$1.05*10^{-6}$ @ 60 °C-100%RH	Apply for OLED device Show no black spot @ 85-85%RH	[15]
ALD Al_2O_3/graphene	$2.0*10^{-3}$ @ 85 °C-85%RH	Apply for OELD device Show no black spot before and after 24h @ RT, ambient	[16]
PDMS/metal foil (Fe-Ni metal foil)	$5.5*10^{-4}$ @25 °C-40%RH	Apply for OELD device Half lifetime for 116.5h @ RT, ambient	[18] \
PDMS/Grapphene/PET (Graphene : 6 dyad)	$1.78*10^{-2}$ @25 °C-45%RH	Apply for OLED device Half lifetime for 70.7h @ RT, ambient	[19]
PDMS	Not mentioned	Use Carbon as electrode Apply for Perovskite device $MAPbI_3$ perovskite, conventional structure For 3000h @ RT, ambient	[20]
ALD Al_2O_3	$1.84*10^{-2}$ @45 °C-100%RH	Apply for Perovskite device $(HC(NH_2)_2PbI_3)_{0.85}(CH_3NH_3PbBr_3)_{0.15}$ conventional structure For 7500 h @ 50%RH under room temperature	[17]
ALD AlO_x/PDMS	$5.1*10^{-3}$ @45 °C, 65% RH	Apply for Perovskite device $(HC(NH_2)_2PbI_3)_{0.85}(CH_3NH_3PbBr_3)_{0.15}$ Conventional structure	Our present work

		For 300 h @ 45 ℃, 65% RH	

Table S2. Test conditions for AlOx deposition in the ALD chamber. Groups (A, B, and C) are to examine the effect of TMA pulse time water pulse time and cycles, respectively.

Group	Chamber Temp. (°C)	TMA precursor Temp. (°C)	TMA precursor pressure (mTorr)	Purging amount of Ar (sccm)	H_2O pressure (mTorr)	Process time (s) (TMA-Ar-H_2O-Ar)	Total cycle
A	95	30	65	100	50	**0.5**-10-1-15	100
						1.0-10-1-15	100
						3.0-10-1-15	100
B	95	30	65	100	50	1-10-**0.5**-15	100
						1-10-**1.0**-15	100
						1-10-**3.0**-15	100
C	95	30	65	100	50	1-10-1.0-15	**100**
						1-10-1.0-15	**200**
						1-10-1.0-15	**400**

Table S3. XPS parameters of AlO_x and PDMS/AlO_x sample

	Elemental peak	Atomic %	Chemical bonding	Binding energy (eV)	FWHM (eV)	Area CPS. (eV)	Relative Area %
AlO_x	Al 2p	60.35	Al-O	74.45	1.52	43125.95	100
AlO_x	O 1s	39.65	Al-O	531.30	2.16	227732.96	75.41
			Al-OH	532.60	1.96	74277.73	24.59
PDMS/AlO_x	Al 2p	53.37	Al-O	74.45	1.47	19390.37	76.97
			Al-OH	75.20	1.32	5801.23	23.03
PDMS/AlO_x	O 1s	30.52	Al-O	531.30	1.54	86928.67	49.36
			Al-OH	532.60	1.29	76129.25	40.21
			O-Si-O	533.00	1.77	49134.19	10.43

Reference

[1] G. Nisato, H. Klumbies, J. Fahlteich, L. Müller-Meskamp, P. van de Weijer, P. Bouten, C. Boeffel, D. Leunberger, W. Graehlert, S. Edge, S. Cros, P. Brewer, E. Kucukpinar, J. de Girolamo and P. Srinivasan, *Organic Electronics*, 2014, **15**, 3746-3755