Electronic Supplementary Material (ESI) for Materials Horizons.
This journal is © The Royal Society of Chemistry 2023

Supporting Information

Study of Mechanical Degradation of Freestanding ALD Al_2O_3 by Hygrothermal Environment and Facile Protective Method for Environmentally Stable Al_2O_3: Toward Highly Reliable Wearable OLEDs

Sangmin Lee[†,1], *Yongmin Jeon*[†,2], *Seung Jin Oh*[1], *Sun-Woo Lee*[1], *Kyung Cheol Choi*[3,]* *and Taek-Soo Kim*[1],* ,*Jeong Hyun Kwon* [4],*

Sangmin Lee, Seung Jin Oh, Sun-Woo Lee, Taek-Soo Kim

[1]Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

Yongmin Jeon

[2]Department of Biomedical Engineering, Gachon University, Seongnam 13120, Republic of Korea

Kyung Cheol Choi

[3]School of Electrical Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

Jeong Hyun Kwon

[4]Department of Display and Semiconductor Engineering, Sun Moon University, Choongcheongnam-do, Asan, 31460 Republic of Korea

[†] These authors contributed equally to this work.
E-mail: love6539@sunmoon.ac.kr (Jeong Hyun Kwon), tskim1@kaist.ac.kr (Taek-Soo Kim), kyungcc@kaist.ac.kr (Kyung Cheol Choi)

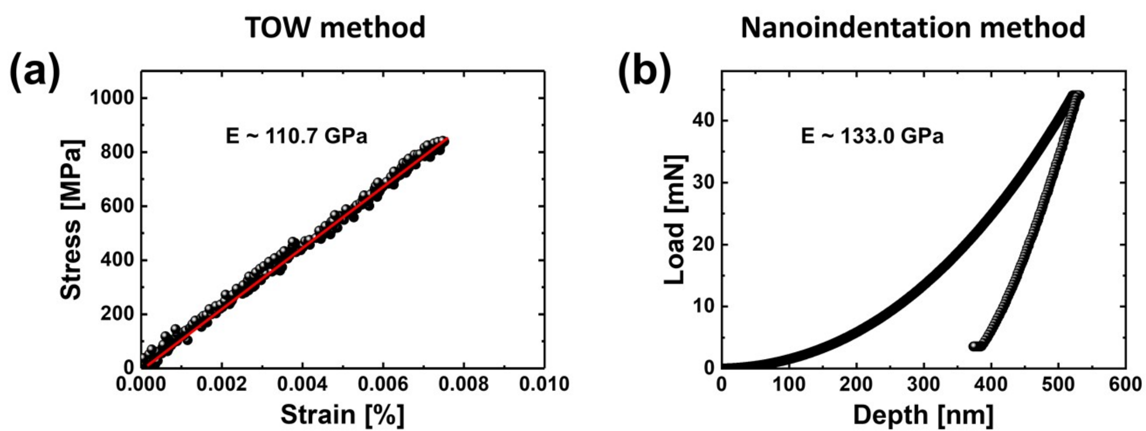


Figure S1. Elastic modulus of the ALD Al_2O_3 film measured by (a) the free-standing tensile testing method and (b) nanoindentation method, respectively.

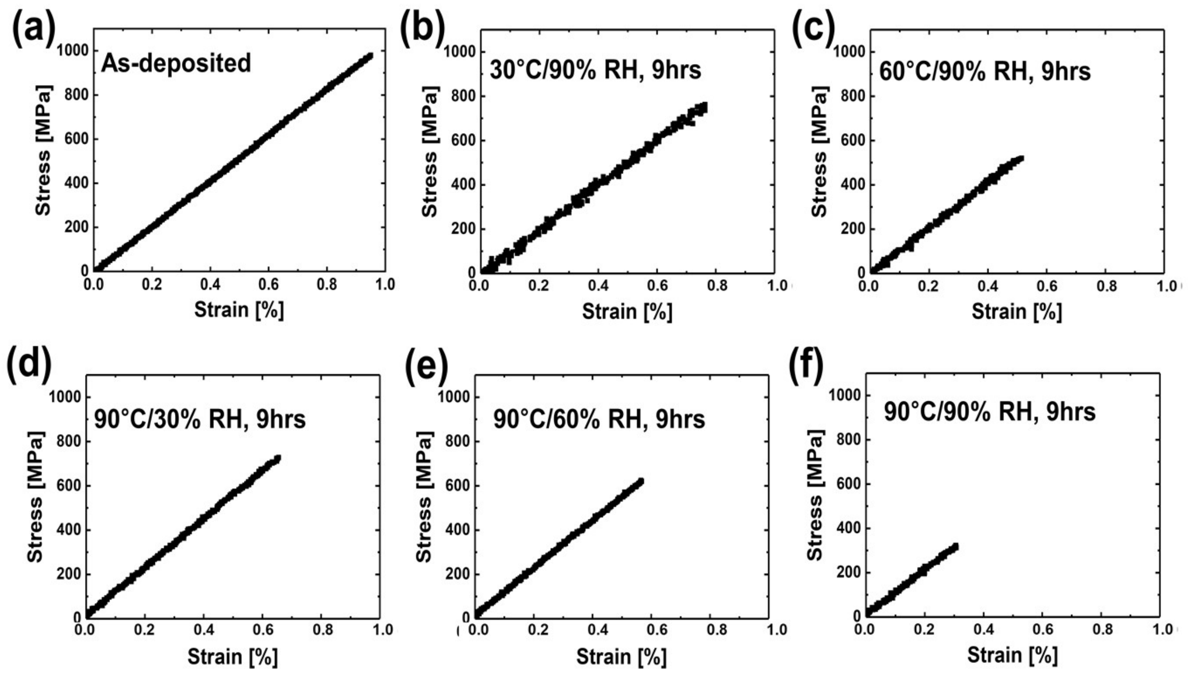


Figure S2. Strain-stress curves of a) as-deposited Al_2O_3, (b) Al_2O_3 after exposure to 30°C/90% RH, (c) Al_2O_3 after exposure to 60°C/90% RH, (d) Al_2O_3 after exposure to 90°C/30% RH, (e) Al_2O_3 after exposure to 90°C/60% RH, (f) Al_2O_3 after exposure to 90°C/90% RH for 9 h.

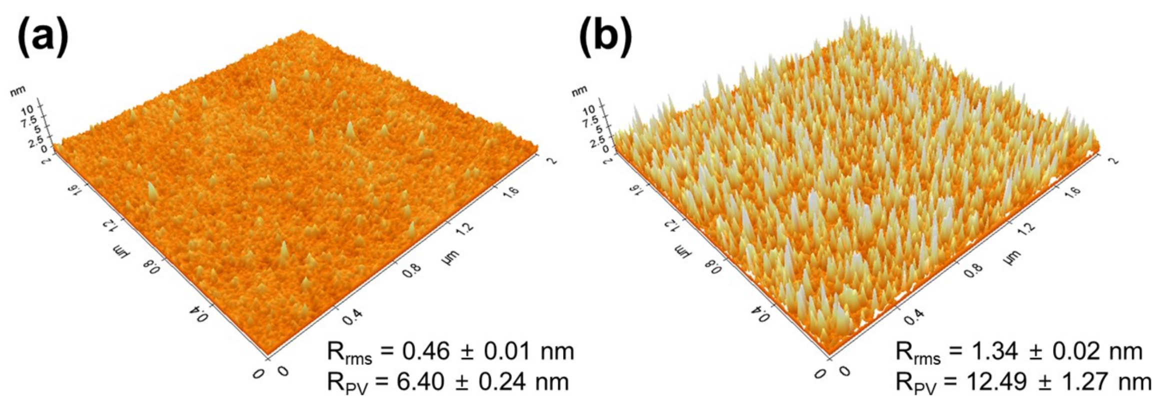


Figure S3. AFM images of (a) as-deposited Al_2O_3 and (b) Al_2O_3 exposed to 90°C/90% RH for 9 h.

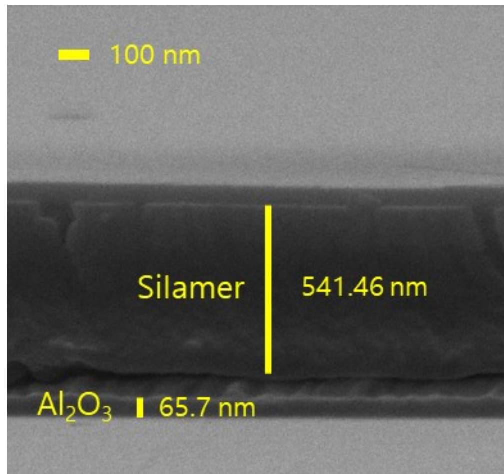


Figure S4. SEM cross-sectional image of the Al2O3/silamer bilayer.

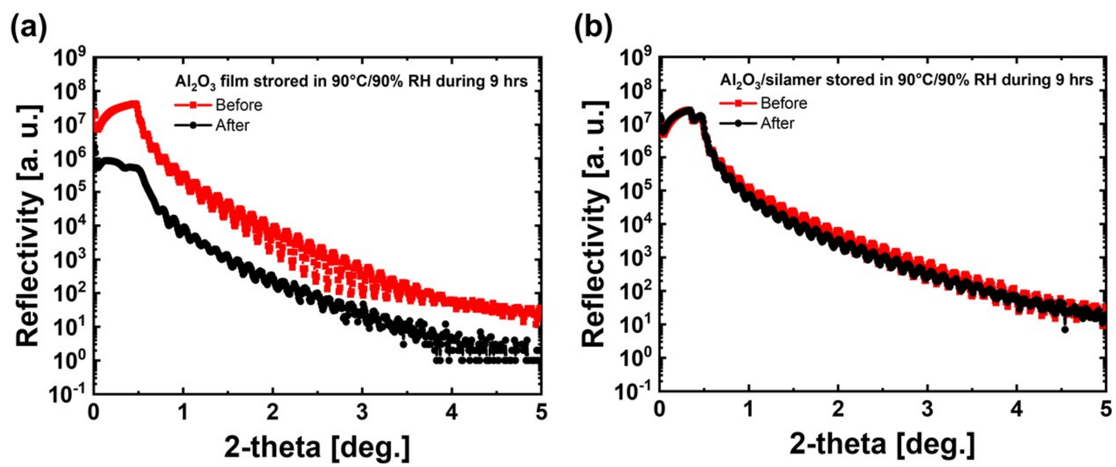


Figure S5. XRR measurements of (a) Al_2O_3 single layer and (b) Al_2O_3/silamer bilayer before and after exposure to the environment of 90°C/90%RH for 9 h.

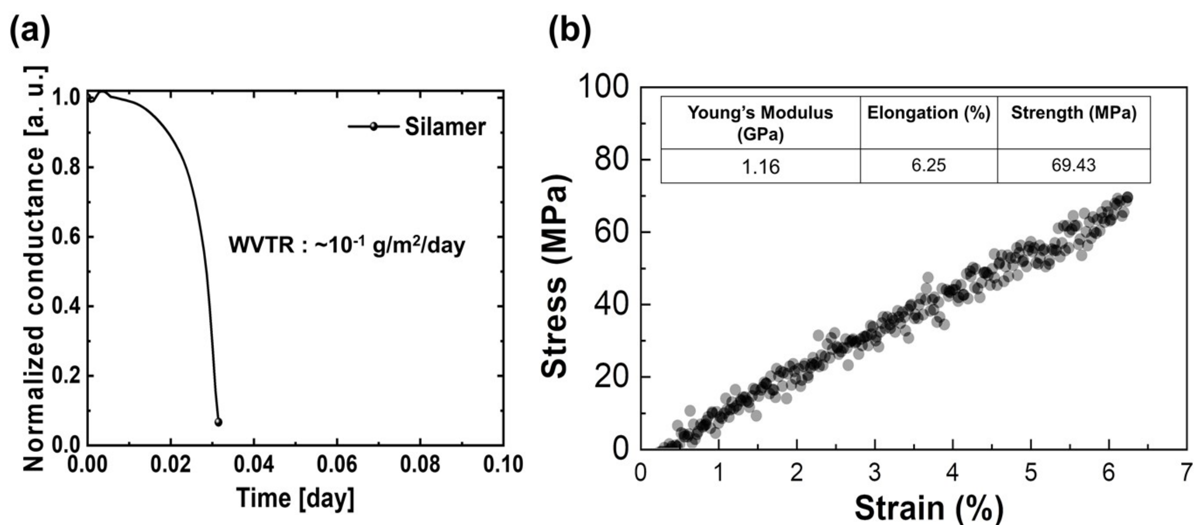


Figure S6. (a) Ca test result of the silamer layer obtained in 30°C/90% RH. (b) Stress-strain curve of the silamer layer measured by free-standing tensile test. Inset: Measured Young's modulus (E), elongation (ε), and strength (S) values of the free-standing silamer layer.

The ALD Al_2O_3 film is easily degraded under harsh conditions owing to its poor environmental stability, which significantly degrades the reliability of devices and films, including Al_2O_3 films. A silamer is a polymer with a layered SiO_2 chain in a mixed base of Si:glycidoxy-propyl trimethoxysilane (Si:GPTMS) and tetraethyl orthosilicate (TEOS) prepared using the sol-gel method. TEOS functions as an adhesion promoter and silane coupling agent during thermal curing after spin coating on the ALD Al_2O_3 film.

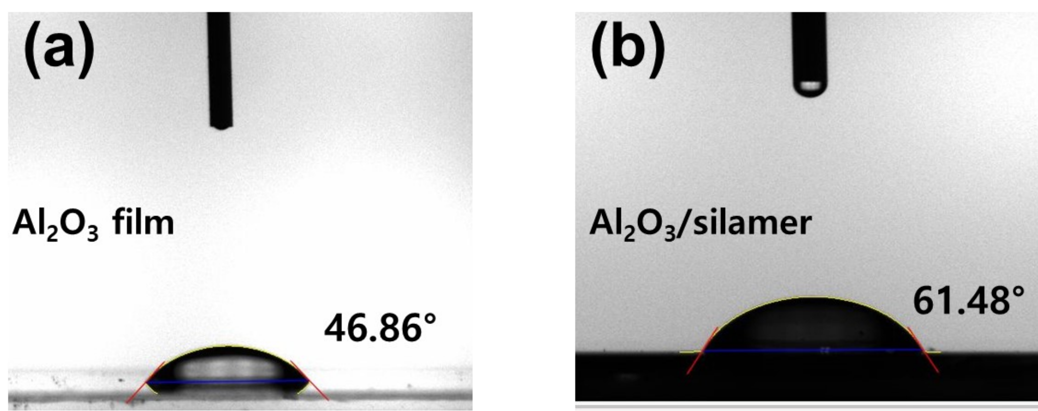
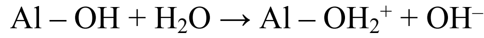


Figure S7. Water contact angle measurements on Al_2O_3 and Al_2O_3/silamer surfaces.

Table S1. Calculated XRR data of Al_2O_3 and Al_2O_3/silamer before and after the aging test.

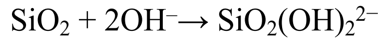
Aging test	Structure	Thickness [nm]	Density [g/cm^3]	Roughness [nm]
Before	Al_2O_3	65.58	2.84	0.75
After		Unable to calculate		
Before	Al_2O_3/silamer	66.19	1.39/2.81	0.53/0.58
After		65.73	1.53/2.83	0.59/0.99

The density and surface roughness of the pure Al_2O_3 film were 2.84 g/cm^3 and 0.751 nm, respectively. However, the XRR curve of the degraded Al_2O_3 film changed significantly compared with that of the pure Al_2O_3 film. Especially, significant changes were observed in the 2-theta region of less than 0.5 degrees with differences in absolute reflectivity values. These changes make it impossible to calculate the density and surface roughness from the XRR graph, implying severe degradation. The thickness, density, and interface roughness of the Al_2O_3 film protected by the silamer layer showed minimal difference from 66.19 nm, 2.81 g/cm^3, and 0.58 nm to 65.73 nm, 2.83 g/cm^3, and 0.99 nm, respectively.



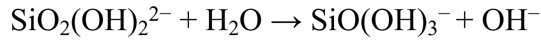
$$Al - OH + H_2O \rightarrow Al - OH_2^{+} + OH^{-}$$

(reaction 1: basification of Al_2O_3 surface)



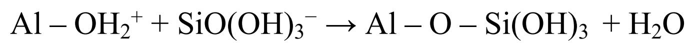
$$SiO_2 + 2OH^{-} \rightarrow SiO_2(OH)_2^{2-}$$

(reaction 2: formation of deprotonated silicic acid)



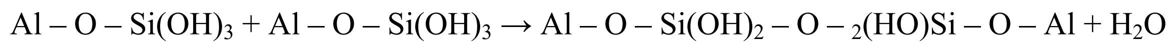
$$SiO_2(OH)_2^{2-} + H_2O \rightarrow SiO(OH)_3^{-} + OH^{-}$$

(reaction 3: Protonation of silicic acid)



$$Al - OH_2^{+} + SiO(OH)_3^{-} \rightarrow Al - O - Si(OH)_3 + H_2O$$

(reaction 4: silicification process at the interface)



$$Al - O - Si(OH)_3 + Al - O - Si(OH)_3 \rightarrow Al - O - Si(OH)_2 - O - {}_2(HO)Si - O - Al + H_2O$$

(reaction 5: formation of aluminate phase through condensation reaction)

These five equations explain the formation of the aluminate phase. In Reaction 1, the hydroxide ions are generated as a byproduct of the reaction with water on the surface of Al_2O_3 and accelerate the dissolution of SiO_2. The primary aluminate phases formed through the silicification reaction between silicic acid and basic aluminum hydroxide were produced through the deprotonation and protonation processes shown in Reactions 3 and 4, respectively. The aluminum hydroxide of the weak base formed through Reaction 1 acted as intermolecular chains between them. Finally, through the condensation reaction, a continuous aluminosilicate layer of Al–O–Si was formed at the interface. Strong interfacial bonding made it possible to address the reliability issue related to the environmental degradation of ALD Al_2O_3 films.