Accelerated electro-chemical delamination test for the durability of transparent conductive oxide (TCO) glass

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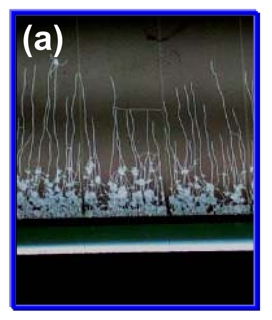
Introduction

The electro-chemical delamination (ECDL) test was developed as an accelerated method to evaluate the propensity of the TCO delamination from the glass substrate. [1],[2] The test (~ 0.5 hour) involves heat and voltage bias to rapidly drive Na^+ ion from the glass to the TCO layer to generate stress, which eventually results in cracking of the coatings (Fig. 1.) The ECDL performance relies on test temperature, humidity, and polarity, which also affect the durability of a PV system. The objective of this test is to evaluate if TCO glass can survive the 20 years of warrantee time of the PV module. [3],[4] However, non-standardized test procedure and a lack of database relating the ECDL results to TCO long-term performance make it difficult to fulfill this goal. Future work with the collaboration between TCO glass manufacture and PV module developer is a necessity to improve this TCO adhesion test.



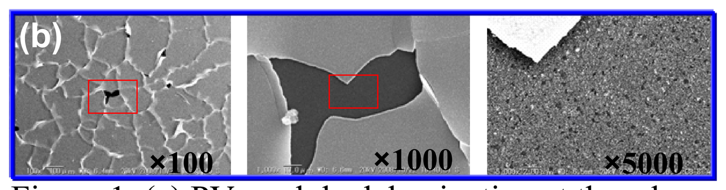


Figure 1. (a) PV module delamination at the edge due to moisture penetration and high voltage bias. (b) TCO coating delamination after ECDL test, which mimic PV module operating conditions.

Test methodology

The schematic diagram of ECDL test equipment is shown in Fig. 2, which includes a hot plate and a voltage source to rapidly drive Na^+ ion from the glass substrate to the TCO layer. The general test procedure includes the following steps:

- the sample is heated at 185 ˚C and a 100 V positive bias voltage is applied to the non-coated side for 15 min;
- the sample is then kept at room temperature within a humidity chamber (50% RH);
- after 5 min in the humidity air, the TCO coating is scratched with a razor blade to generate a path for water vapor to reach the TCO/glass interface. Scratching also creates defects that initiate delamination in damaged coatings;
- observation of the scratched coatings within the following 10 min differentiates coatings with bad adhesion from the good ones.

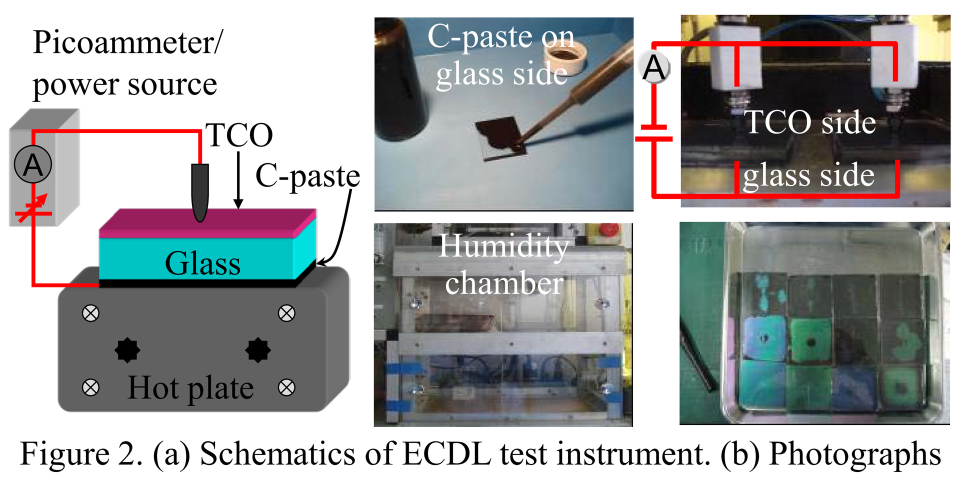
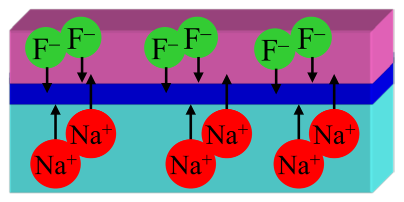


Figure 2. (a) Schematics of ECDL test instrument. (b) Photographs of the ECDL setup and the test procedure.

Results

❖ Analysis of delaminated samples reveals the weak interface:

<u>Why coating delaminates after ECDL test?</u>



Under positive bias, alkaline ions in glass and F^- in SnO_2:F were driven towards TCO/glass interface:

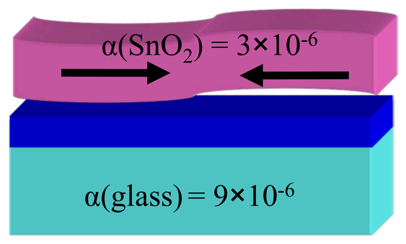
(a) Chemical reactions at interface decrease interface adhesion: [1]

$$F^- + H_2O \rightarrow HF + OH^-$$
$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

$$Na + H_2O \rightarrow NaOH + H$$
$$SnO_2 + 4H \rightarrow Sn + 2H_2O$$

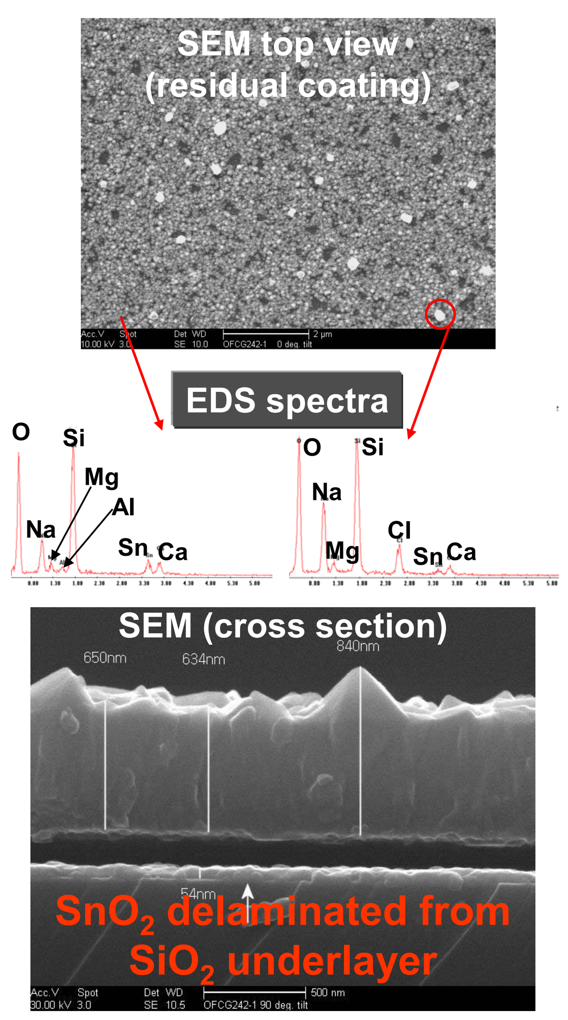
(b) Due to different thermal expansion coefficient ($\Delta\alpha$) between glass and SnO_2, compress stress is built up in the coating when it is cooled down, for instance, from ~550 ºC to ~20 ºC.

When compression stress in the TCO coating becomes larger than the interfacial adhesion, coating delaminates: [5]

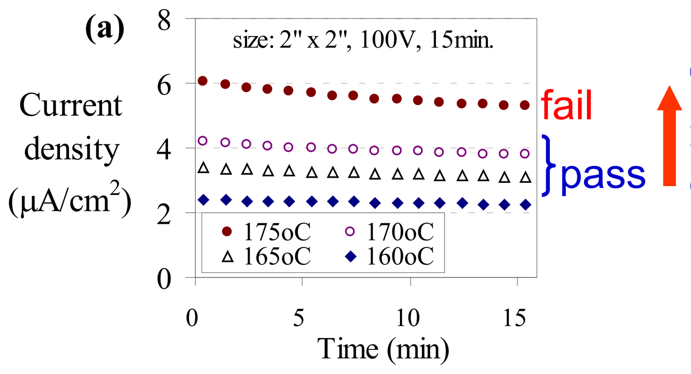


Mismatch strain:
$$\varepsilon = \Delta\alpha \cdot \Delta T$$

Mismatch stress is ~0.98 GPa:
$$\sigma_{therm} = E \cdot \varepsilon / (1 - \nu)$$



❖ ECDL test result is sensitive to test conditions that determine the total amount of charge passing through the TCO/glass interface (Fig.3.)



Temperature ↑, mobility of alkaline ion↑, delamination current↑.

<u>Glass resistivity vs. Temp:</u>

$$Log\rho_{(T)} = A + B/T$$
$$\rho_{(T=175\ ^\circ C)} \sim 6.3 \times 10^8\ ohm\text{-}cm$$
$$\rho_{(T=160\ ^\circ C)} \sim 3.2 \times 10^8\ ohm\text{-}cm$$

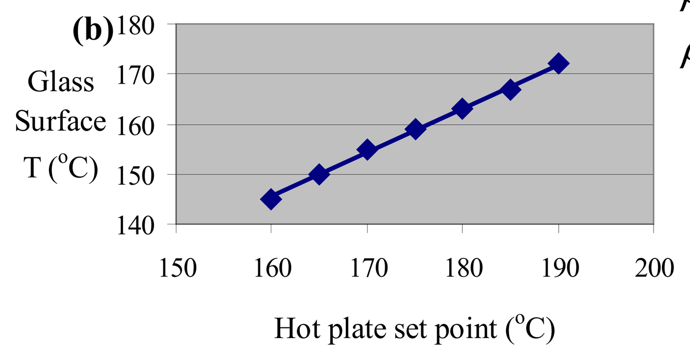


Figure 3. (a) Delamination current density at different glass surface temperature. (b) Temperature difference between glass surface and hot plate surface.

❖ Improve reliability of the test results:

- standard equipment setup with regular calibration;
- consistent test procedure;
- clear definition of failure;
- optimized procedure, such as scratching the coating [6] after ECDL test (Fig. 4.).

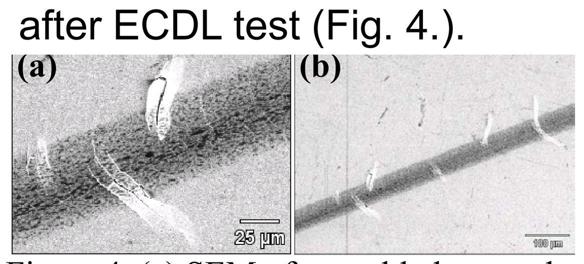


Figure 4. (a) SEM of razor blade scratch after ECDL. (b) SEM of the same area of the coating after 7 days.

❖ Enhance the TCO adhesion to glass substrate:

- Chemical approach to minimize alkaline ion transfer – glass resistivity (Fig. 5), Na blocking layer; [7]
- Mechanical approach to increase interface strength (Fig. 6), and decrease stress in TCO coating.

Sample	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO
clear	72.0	1.9	0.1	**13.0**	**1.2**	7.6	4.0
low iron	72.0	1.8	0.0	**14.0**	**0.0**	7.6	3.8

SiO_2/ITO by sputtering	resistivity	low iron	mixture	clear
		low	medium	high
	100V	fail	pass	pass
	50V	pass	pass	pass

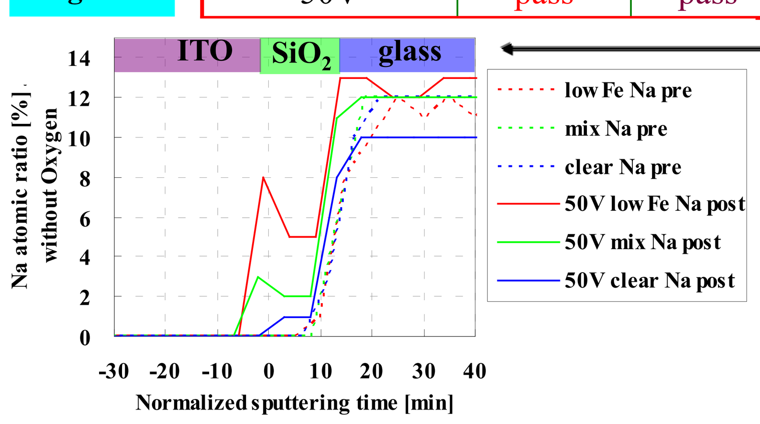
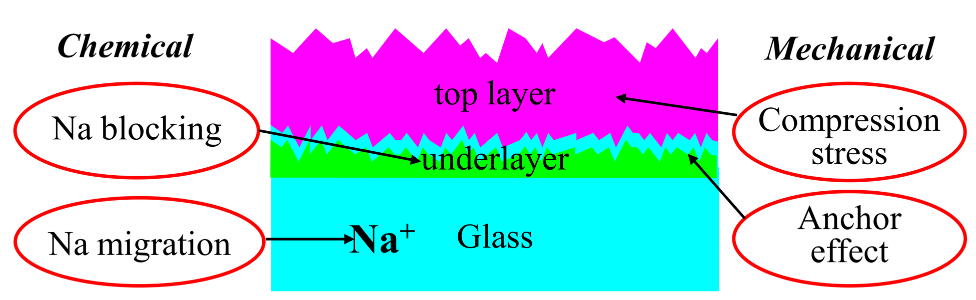


Figure 5. XPS step profile of Na distribution before and after ECDL test on different glass substrate.



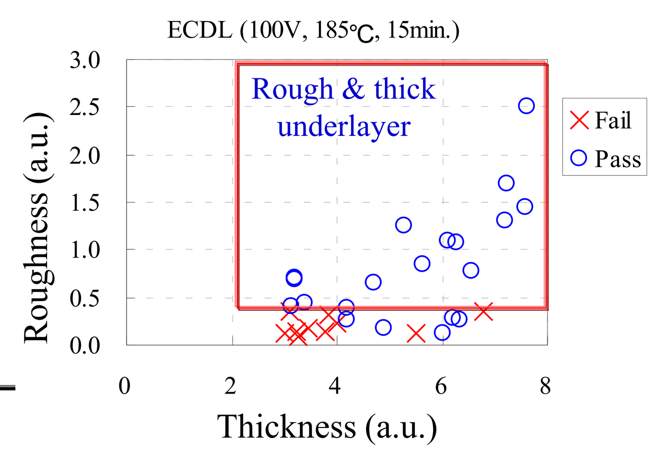


Figure 6. Effect of underlayer thickness and roughness on SnO_2 adhesion. [8]

Conclusions

ECDL test has been demonstrated to be an effective method for screening TCO/glass adhesion property (Fig. 7), especially in the case when the TCO glass is subjected to high voltage during normal PV module operation. SEM and XPS analysis on delaminated coating shows Na^+ migration from glass to TCO layer plays a key role in diminishing interfacial bonds, which eventually leads to the detachment of the coating from glass substrate. Based on the understanding on delamination mechanism, two approaches were proposed from chemical and mechanical perspectives to limit Na^+ transport, and to increase interface strength. The high sensitivity of the test results to ECDL test conditions, especially to temperature, also reveals the challenge in establishing a common base for direct comparison of TCO adhesion.

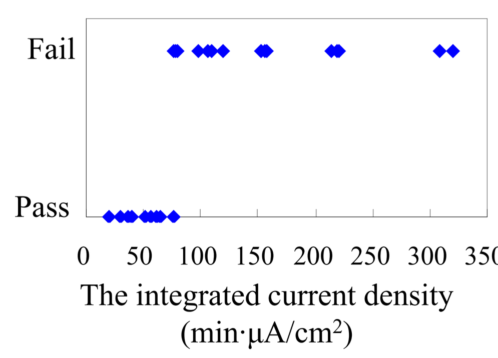


Figure 7. Integrated current density per unit area shows how much charge passes through the glass/TCO interface. A threshold charge can be calculated from the ECDL test, which can be used to predict the lifetime of the coating under normal condition.

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For further question

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