

Stress Modulated Flexible Oxide Electrode and Water Vapor Transmission Observation of Cracked Oxides

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Transparent conducting oxides (TCOs) have been widely used as the electrodes for commercial organic devices for their superior electrical and optical characteristics. Nevertheless, TCOs are facing challenges for serving as an flexible electrode due to their brittle nature [1-3]. In this article we presented a new concept to fabricate indium tin oxide (ITO) film with high flexibility without the combination with metals. The idea is to yield a film consisting of multiple, intentionally cracked ITO layers, named pre-cracked ITO. In this way, the ITO film is expected to develop no new cracks with time within an allowed stress condition when being bent. Unlike in a single ITO layer, where the cracks can possibly impede all the charge carriers, the charge carriers in a pre-cracked ITO film can travel between electrical networks between the cracked ITO layers. With this respect, this study aims to discover how much the flexibility of an ITO film can be improved with the stress modulation of the pre-cracking films.

Figure 1 shows the electrical resistance variation of ITO/PET during a dynamic bending test of 1,000 cycles for the 1L ITO (one single layer) with and without thermal annealing. It can be seen that the resistance of the as-deposited ITO film increases rapidly from its initial resistance of $\sim 60 \Omega$ to over $17,000 \Omega$ at 1,000 cycle, whereas the resistance of the thermally annealed ITO film reaches 400Ω approximately. The SEM images inset in the figure reveal the as-deposited ITO film not only cracked but also delaminated from PET, while the thermally annealed ITO cracked with no delamination. The cause of the more serious cracking of the as-deposited film is believed to be due to the high internal stress formed during sputter deposition, generally a compressive stress with the sputter conditions applied [4]. The thermal annealing helps to release internal stress and allows ITO film to tolerate higher external bending stress. The result gives a clear message that the internal stress in a film can considerably degrade the mechanical flexibility.

Figure 2 (a) shows the resistance variation during a 1000-cycle bending test for 1L – 5L stacking ITOs of totally 200 nm thick. These ITO films were coated with the PET substrates flat placed during sputter processing and named flat-coated ITOs. It clearly reveals that all the stacked (2L ~5L) ITOs perform deteriorated flexibility as their electrical resistances increase with bending cycles more seriously than the 1L ITO. The resistance after 1,000 bending cycles is particularly high for the 3L and 5L ITOs with $R = 4,140 \Omega$ and $2,510 \Omega$, respectively. The resistance deterioration is less severe for the 2L and 4L ITOs with $R = 500 \Omega$ and 650Ω , respectively, compared with 407Ω of the 1L ITO. The results indicate that the stacked and flat-coated ITOs built more internal stress during the coating/cracking cycles compared with the 1L ITO. And therefore, the 3L and 5L ITOs seem to have higher internal stresses than 2L and 4L ITOs. The figures also revealed that the resistance in any case increases greatly in the first 100 bending cycles, suggesting cracking develops rapidly in the beginning of bending. It is likely the films with lower internal stress can release stress quickly through the generation of cracks, whereas the films with higher internal stress would continue to develop cracks until all the stress can be fully released.

To reduce the film stress, we curved PET sheets at a curvature (r_d) of 8 mm in the course of ITO depositions, and named the ITO/PET the curve-coated ITO. Fig. 3 (b) shows the resistance variation of the 1000-cycle bending test for 1L – 5L ITOs. It can be seen that all the curve-coated ITOs exhibit elevated flexibility in comparison with those flat-coated. In comparison with the 1L ITO, the 5L ITO performs better in flexibility while the 2L ITO shows similar resistance variation, and the 3L and the 4L ITOs remain degraded. The results suggest that the curve coating helps to lower the internal film stress and consequently enhances the flexibility of pre-cracked ITO films.

The water vapor transmission of the stress modulated pre-cracked ITO films were observed using the optical calcium test. From Fig. 3 one can see that after 1 hour test the water vapor penetrated initial ITO in a randomly dotted pattern, while the water vapor penetration is mainly through cracks in the 5L pre-cracked ITO film. We found the higher the density of the cracks, the faster the calcium film oxidation rate, indicating the water vapor transmission rate (WVTR) is associated with the crack density. The WVTR of the 5L ITO is $9.04 \times 10^{-1} \text{ g/m}^2/\text{day}$ compared with that of the 1L ITO of $1.31 \text{ g/m}^2/\text{day}$. It can be said that the use of pre-cracked ITO helps to improve both the bending mechanical properties and the gas blocking rate.

In conclusions, multiple stacked ITO films with stress modulated and pre-cracked layers have shown prominent enhancement in flexibility. The enhanced flexibility is believed to be due to the electrical networking yielded between the pre-cracked layers and the release of internal film stress. The reduction of the internal film stress of ITO films leads to a crack-free surface after 10,000 bending cycles, showing the potential for a single ITO material to serve as an electrode for flexible organic electronics.

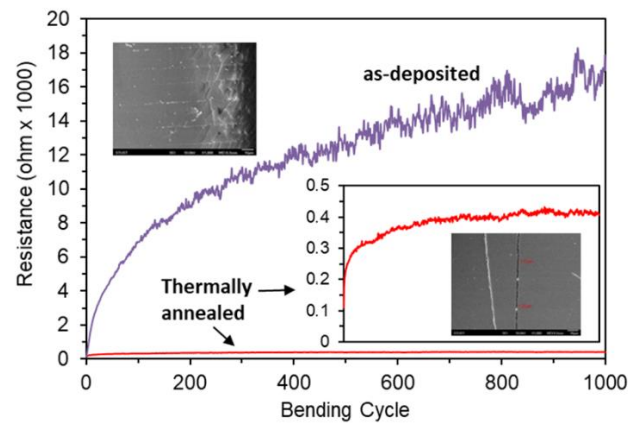


Fig. 1 the electrical resistance variation of ITO/PET during a dynamic 1,000-cycle bending test for 1L ITO with and without thermal annealing

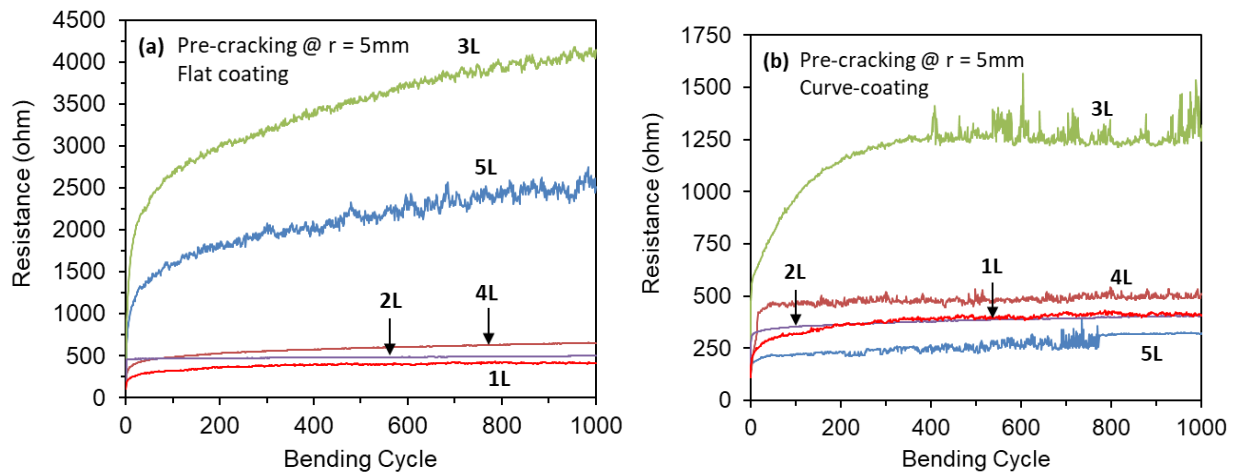


Fig. 2 the resistance variation during a 1000-cycle bending test for 1L – 5L ITOs, (a) flat coating, (b) curve coating.

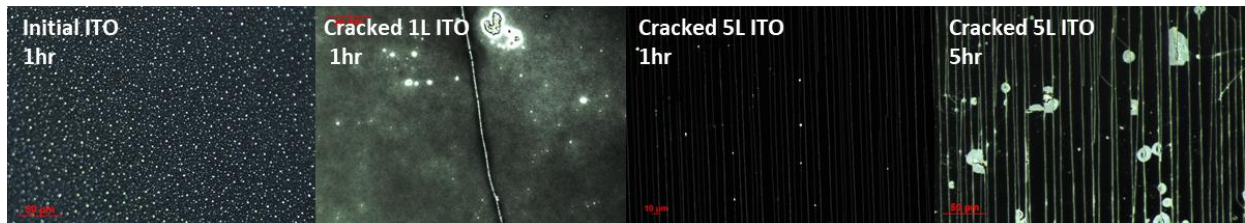


Fig. 3 water vapor transmission of 1L and pre-cracked ITO films observed using the optical calcium test.

References

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