

APPLICATIONS BULLETIN

Nanoindentation and Nanoscratch of Oxide Coatings on Thin Film Polymer Substrates

//// Introduction

The reliability of novel flexible opto-electronic devices depends heavily on the resilience of a thin ceramic oxide layer deposited on a polymer substrate. Currently, one of the most popular combinations consists of a thin layer of Indium Tin Oxide (ITO) on a polyester substrate, such as polyethylene terephthalate (PET). The ITO layer, usually around a few hundred nanometers in thickness, is very susceptible to cracking. As this layer experiences cracking and delamination from the substrate, the resistance of this layer sharply increases and it is rendered useless.

Characterization of the mechanical properties of this oxide layer after deposition is very important. The properties of ITO deposited on glass have been previously investigated, but because the ITO layer has an amorphous structure, the properties of the ITO can be quite different than when deposited on glass. A large mismatch in modulus between the ITO and the polymer substrate can also affect adhesion to the substrate and the measured hardness values. For this reason, indentation and scratch testing of the ITO-coated PET system is very valuable, but straightforward testing might not always be an option.

There are a number of challenges when performing both indentation and scratch testing on a system consisting of a thin hard coating on a soft polymeric substrate. Care must be taken to ensure substrate effects do not influence the coating data.

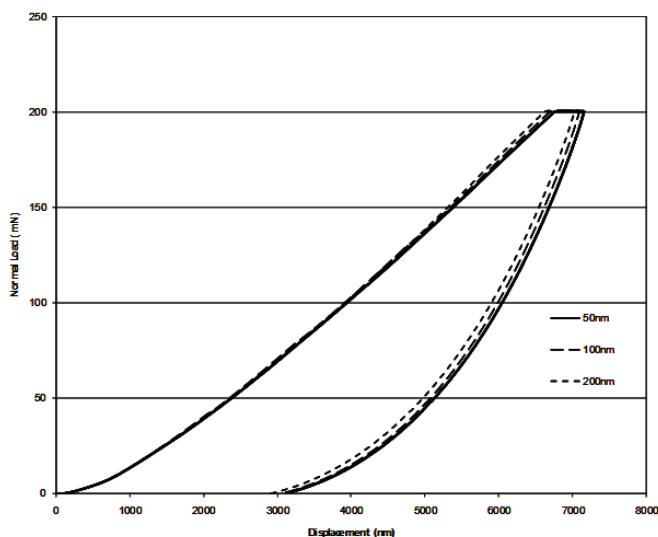


Figure 1: Load depth curves for 3 coating thicknesses.

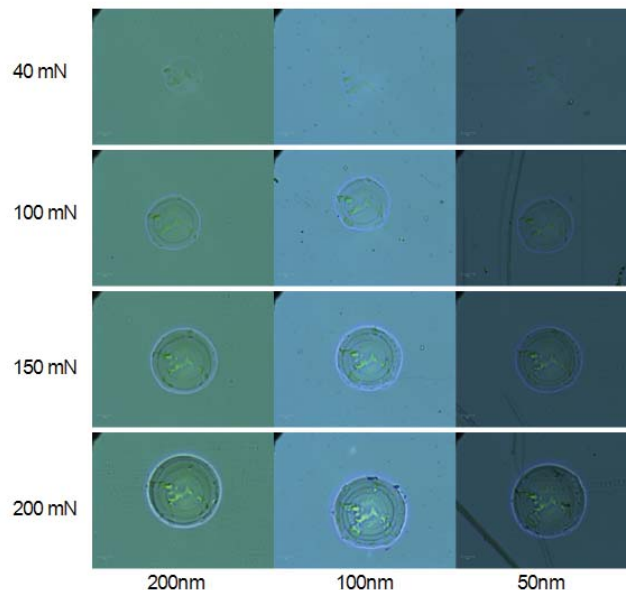


Figure 2: Optical micrographs of residual indents for 4 applied normal loads and 3 coating thicknesses (1000x magnification).

The techniques described here include nanoindentation with a spherical indenter to promote circumferential cracking of the brittle layer and nanoscratch testing to promote adhesive failure.

//// Experimental

For nanoindentation testing, a 20 μm spherical indenter was loaded to normal loads up to 200 mN with a pause of 10 seconds. The goal of this style of indentation testing was to promote cracking of the ITO layer. In all cases, the first visible crack appeared at approximately 40 mN. At 100 mN a second circumferential crack was observed, while at 150 mN a third crack was present. Radial cracking was also observed at a load of 200 mN for the coating thicknesses of 50 nm and 100 nm. Severe damage of the 50nm thick coating was observed at 200mN. Optical micrographs of each indent can be seen in Figure 2.

Penetration depths of several microns were observed for the films. The load-depth curves presented in Fig. 1 show a small variation between samples due to coating thickness. The diameter of each crack was measured optically. The primary circumferential crack diameter for all samples and loads was equal to the diameter of the indenter itself (20 μm). This shows cracking was promoted by the compliance of the polymeric substrate.

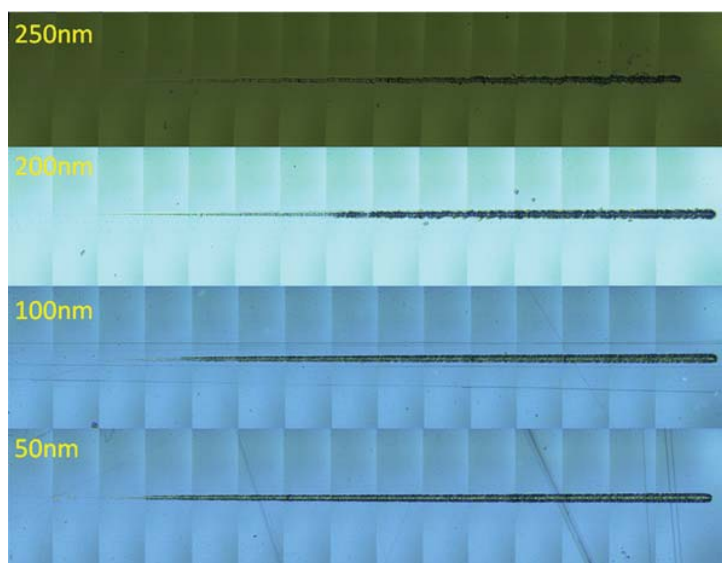


Figure 3: Panoramic comparison of scratches on each sample, (500x magnification). Applied load range was 0.08 - 5 mN.

As the indenter first makes contact and load is increased, a primary crack is formed. Further loading elastically deforms the substrate while causing cracking and delamination of the ceramic coating. Future work will model this contact with the goal of understanding this failure mechanism in more detail.

Nanoscratch testing was performed using a 5 μm radius spherical diamond indenter. Samples were adhered to glass slides for testing. Low-load scratching was performed using the High Resolution cantilever of the Nano Scratch Tester (NST). Critical loads were determined using optical methods and were compared for several coating thicknesses.

Two primary failure mechanisms were observed for all samples. The first mode of failure during testing was rupture of the ITO layer. Further failure occurred in the form of spallation of the coating and scarring of the PET substrate. A panoramic comparison of a scratch performed on each sample is presented in Figure 3.

Scanning Force Microscopy (SFM) was performed at the critical failure points of the sample with a coating thickness of 250 nm and is presented in Figure 4.

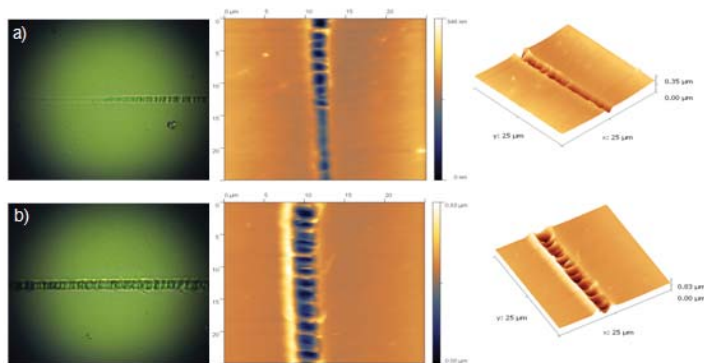


Figure 4: Optical and 2-D and 3-D AFM micrographs of the LC1 (a) and LC2 (b) for the sample with a coating thickness of 250nm.

The load at failure was also plotted against coating thickness and is shown in Figure 4. This graph shows that the failure mechanism of spallation of the coating has a greater dependence on coating thickness than a failure characterized as rupturing.

Scratch width at the critical loads was also measured using optical methods for each scratch and was plotted against film thickness. This plot can be seen in Figure 5. Scratch widths at the critical loads appear to be less dependent on film thickness than the critical load values themselves.

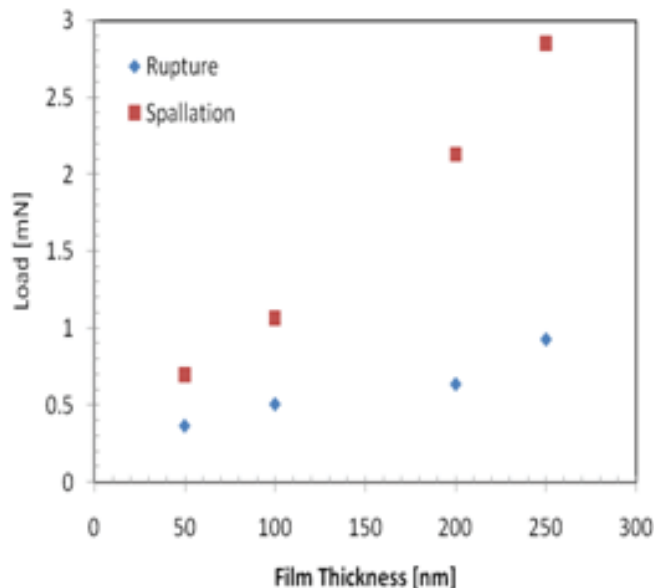


Figure 5: Plot of the load at failure for each failure mechanism as a function of film thickness.

//// Conclusions

When attempting to determine the mechanical properties of a transparent oxide deposited on a thin polyester film, it is necessary to adapt indentation and scratch testing methods. Indentation testing utilizing a spherical indenter to promote circumferential cracking and low-load scratch testing with a high-resolution friction table were used to characterize and compare the mechanical properties of the composite films. Results show that these methods can accurately characterize differences in film thickness. Further developments in these testing methods will allow for a more flexible range of tests that can be conducted on thin composite films. This will allow correlations to be made between laboratory sample testing and the actual in-service performance of devices which utilize ITO technology (e.g., touchscreens, flexible solar cells, flexible LED lighting, etc.)

//// Acknowledgements

Prof. Darran Cairns and Nick Morris of West Virginia University are acknowledged for providing these interesting results.

//// References

- 1) K. Zeng, et al. Thin Solid Films 443 (2003) 60-65
- 2) B. R. Lawn, Journal of Materials Research, Vol 17, No. 12, Dec 2002
- 3) H.Chai et al. Journal of Materials Research, Vol 19, No. 6, Jun 2004

Measurement of Acoustic Emission during Microindentation

Most common microindentation measurements in both bulk and thin film systems focus on the determination of hardness and elastic modulus of the material. However, in many material systems, discontinuities in the load-depth relationship can often be observed, especially in materials where film failure, delamination, dislocation movement or phase change may have occurred. Characterization of certain physical phenomena using acoustic emission can provide an accurate in-situ measurement of both the magnitude and type of event.

Previous studies on the acoustic emission behaviour during indentation of a variety of materials have shown that the speed at which an event occurs can be correlated to the type of event which led to the acoustic release of energy. Since microindentation causes discrete, localized events, the ability to identify each physical event and correlate them to the acoustic behaviour allows a direct comparison between the event and the individual acoustic emission signature.

Acoustic emission is the sudden release of elastic energy into acoustic waves that travel through the material. Traditionally, such waves have been separated into two types of behaviour: burst emission and continuous emission. A burst emission is a discrete packet of waves associated with a single event, whereas continuous emission tends to be an agglomeration of many small interlinked events. The CSM Instruments Microindentation Tester (MHT) incorporates an acoustic emission sensor operating with a frequency of 150 kHz over a dynamic range of 65 dB with amplification up to 200,000x. Such a wide dynamic response enables the sensor to resolve acoustic events in most engineering materials when subjected to instrumented indentation over the applied load range 0.01 - 30 N. The sensor is mounted directly on the indenter housing to minimize losses and its signal is acquired simultaneously with the load and depth signals to give a complete picture of a compressive fracture event.

One of the distinct advantages of acquiring the acoustic signal during microindentation is that it provides an indication of when the acoustic event actually occurs during the experiment. Fig. 1 shows a range of examples of acoustic signatures for microindentations made on a Si wafer with a Vickers indenter. In each case, brittle fracture (cracking) has occurred during the loading portion only. This is an interesting observation because cracking can sometimes also occur during the unloading phase in some materials. In these eight examples, the maximum load (15 N) has been maintained in each case, but the loading rate has been varied over the range 1 - 250 N/min. in order to investigate the influence of loading rate on the severity of cracking.

It can clearly be seen that the fastest loading rate results in the severest cracking, observed both from the level of the acoustic signal and subsequent optical microscopy of the residual indentation. An example of a progressive load multicycle on a Si wafer is shown in Fig. 2. This confirms that cracking occurs only during the loading portion even though the material is being progressively fatigued by increasing the applied load through five steps. Fracture in brittle materials is usually more significant when the load is progressively applied than if a single load-unload cycle (to the same maximum load) was applied.

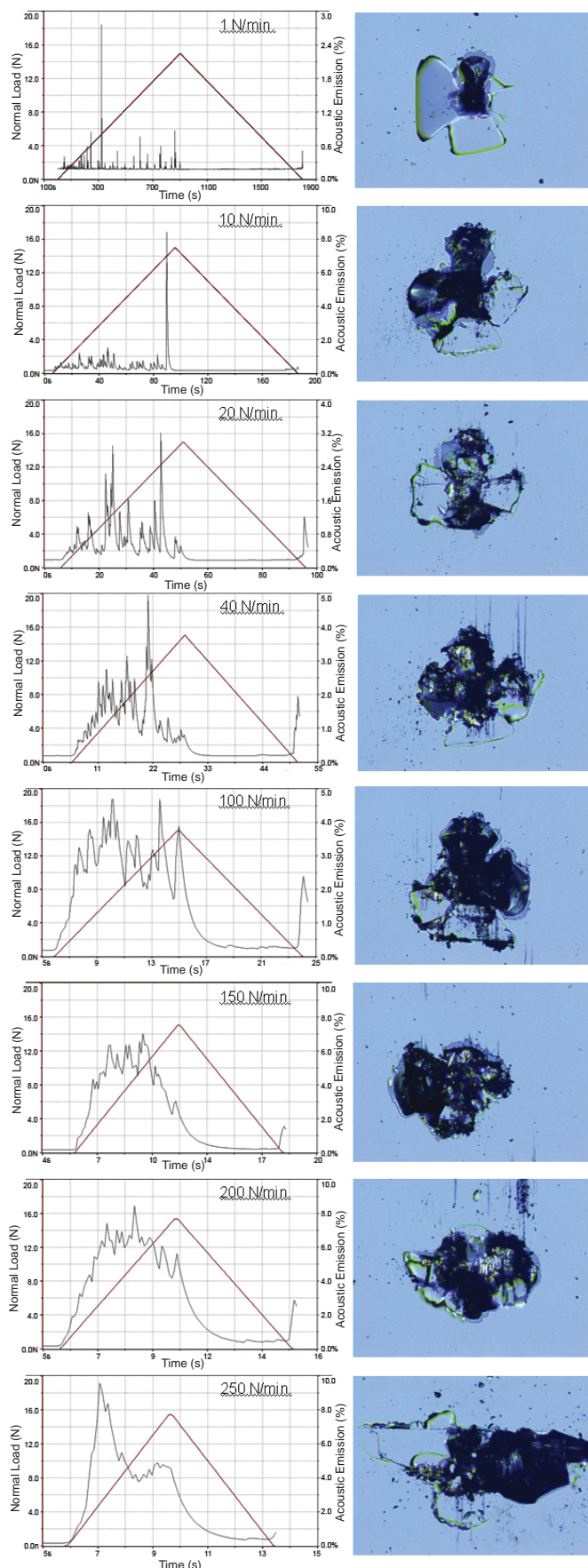


Figure 1: Typical acoustic emission signatures for microindentations made on a Si wafer with applied load of 15 N. Loading rates of 1, 10, 20, 40, 100, 150, 200 and 250 N/min. are shown.

This is because more energy is being channelled into the material in the former case. In some cases, the subsequent acoustic bursts can be stronger than the original burst, and the time between bursts is much greater than the time in which a sound wave can travel across the sample. This leads to the conclusion that the multiple events observed are not merely reflections of the acoustic waves, but are individual events. It should also be remembered that only a fraction of the acoustic energy is picked up by the detector, and only a fraction of the released elastic energy is converted to acoustic energy. Even though the signal is limited by the bandwidth of the sensor used, the ability to arrive at a semi-quantitative measurement of event strength makes it an appealing method of analysis.

Figure 3: Shows the acoustic signature for a microindentation on a Titanium Nitride thin film of thickness 3 µm. Again, the main acoustic events are observed during the loading phase and corresponding cracking is observed around the residual imprint. In the case of a coating, the acoustic signal may give an indication of the bond strength between the coating and the substrate: if the coating is poorly bonded, then little energy may be released during delamination.

Since the elastic energy released during coating delamination can be quantitatively measured (from the load-depth curve) it could be possible to calibrate the energy output of a given sensor to the elastic energy released.

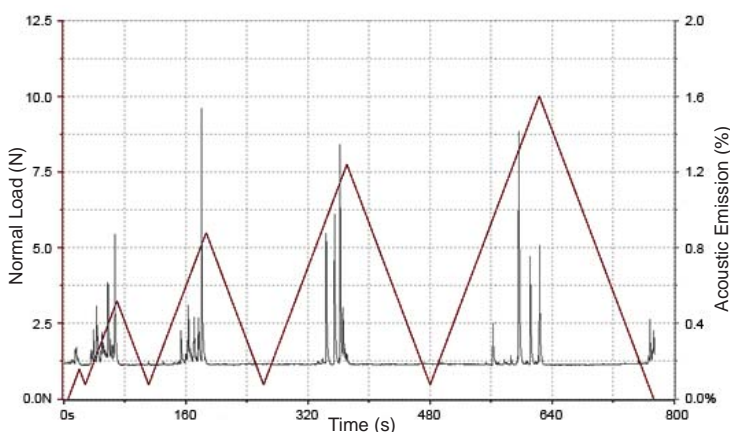
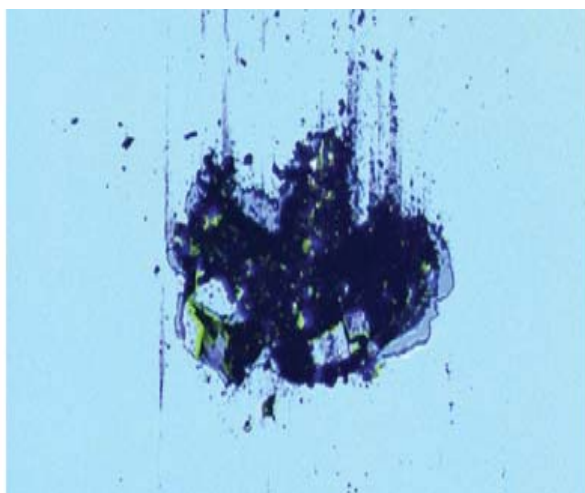


Figure 2: Progressive load multicycle (5 cycles over range 1 - 10 N) with a Vickers indenter on a Si wafer. Acoustic signal confirms cracking during the loading portion of each cycle.

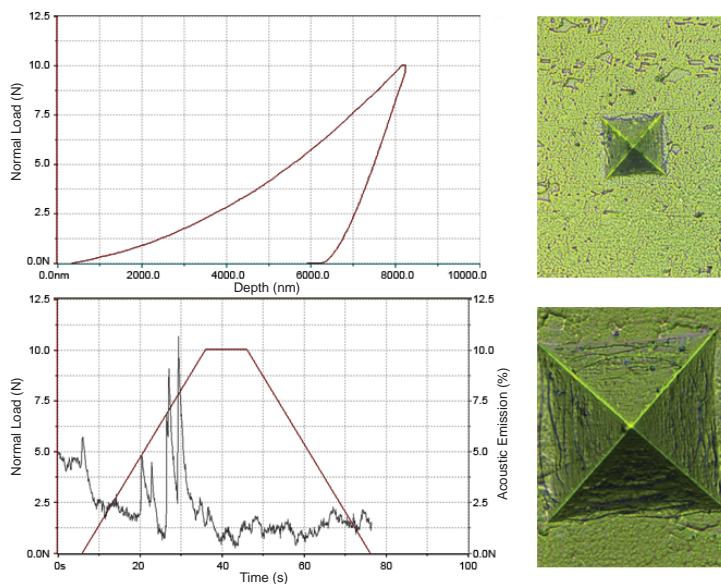


Figure 3: Acoustic signature for a microindentation with applied load of 10 N on a Titanium Nitride (TiN) coating (thickness 3 µm) on a steel substrate.

In any case, acoustic emission measurement shows great promise for revealing the relationship between physical phenomena and the corresponding acoustic emission signal. Such measurement capability will be able to shed some light on the magnitude of a brittle failure event as well as the precise moment when it was initiated.

//// References

- 1) D. F. Bahr and W. W. Gerberich, *J. Mater. Res.*, Vol. 13, No.4 (1998) 1065-1074
- 2) D. F. Bahr, J. W. Hoehn, N. R. Moody and W. W. Gerberich, *Acta Mater.*, Vol. 45, No.12 (1997) 5163-5175



This Applications Bulletin is published quarterly and features interesting studies, new developments and other applications for our full range of mechanical surface testing instruments.

Editor Dr Nicholas X. RANDALL

Should you require further information, please contact:

CSM Instruments Rue de la Gare 4 CH-2034 Peseux Switzerland	Tel: + 41 32 557 5600 Fax: +41 32 557 5610 info@csm-instruments.com www.csm-instruments.com
--	--