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NANO AND MICRO INDENTATION AND SCRATCH TESTS OF COATINGS AND THIN FILMS

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1 Abstract

Based on recent studies, mechanical and tribological properties such as hardness, Young's modulus, friction, and scratch adhesion strength of various coatings and ultra-thin films are reported. These results, obtained using a Universal Nano+Micro Tester UNMT-1, indicate that a substrate effect for ultra-thin films is substantial when using conventional static nanoindentation technique, while negligible with an advanced dynamic nano-indentation. Comparative results of hardness and Young's modulus obtained from various techniques are presented. Also, a means to evaluate friction and adhesion strength of thin films is highlighted, using DLC specimens as an example.

2 Introduction

Evaluation of mechanical and tribological properties of bulk and coating materials is of great importance for design and development of engineering components with enhanced structural and wear performance [1-3]. Traditional indentation tests of bulk materials usually include macro-hardness measurements at high loads of the order of kN. Micro-hardness measurements of coatings and bulk materials are usually performed under relatively low loads of the order of N. As the industrial technology advanced, the characterization technique for mechanical properties of thin films and coating shifted its range from mN to μ N.

Micro-hardness tests are widely used for evaluation of thick coating materials. In recent years, nano-indentation becomes a popular technique, which allows for evaluation of hardness and Young's modulus of films and coatings. The nature of stress distribution in the front of a nano-indenter tip makes the nanoindentation technique vulnerable to a substrate effect for evaluation of ultra-thin films for their mechanical properties. Usually, the indentation depth should be restricted to 5 - 10% of the film thickness to limit the stress field within the thickness of the film and thus, to avoid the substrate influencing the results of such measurements. Such measurements at ultra-shallow depths would require an extremely high accuracy of both depth monitoring and tip calibration. Although AFM-based nano-indentation shows some potential to circumvent such problem, the use of compliant tips limits its applications to soft materials. A novel. Nano-analyzer enables quantitative characterization of ultra-thin films, including hard and super-hard films, at shallow depths with a negligible substrate effect. Nano-analyzer can also perform ultra-shallow nano-scratches and subsequent imaging to

evaluate scratch hardness at nano-level, and mapping of Young's modulus of ultra-thin films with no substrate effect.

Primary objective of the present investigation is to compare different tools and techniques to perform mechanical and tribological tests in micro and nano-level using a single tester. The usefulness of these techniques for effective evaluation of mechanical and tribological properties of bulk and thin film materials is also reported.

3 Experimental

The micro-indentation, micro-scratch, nano-indentation, nano-scratch, and nano-imaging techniques were employed for evaluation of mechanical and tribological properties of numerous bulk, coating and film specimens using the same Universal Nano+Micro Tester model UNMT-1, designed and manufactured by CETR, Inc. The photograph of its nano-head is presented in Figure 1.



Figure 1: Nano-indentation module for UNMT-1

UNMT-1 has several easily interchangeable modules for precision tests of hardness, Young's modulus, friction, and adhesion of bulk, coating and film materials, including:

- traditional micro-indentation up to a load of 1.2 kN, with Rockwell, Vickers, and Knoop indenters according to ASTM E18-05, ASTM E92-82, and ASTM E384-99 standards, respectively. It is capable of performing post-test measurements of diagonals of indentation with an optical microscope as required by Vickers and Knoop hardness test procedures, and of indentation depth with a capacitance sensor for Rockwell hardness test,

- instrumented micro-hardness tests per the ISO 14577-1/02 up to a load of 1.2 kN with the same Rockwell, Vickers, or Knoop indenters, but in-situ monitoring of load and depth and automatic calculations of both instrumented hardness and Young's modulus,
- instrumented static nano-indentation tests per the ISO 14577-1/02 (loads from 0.1 μN to 0.5 N) with Berkovich, conical and cube-corner indenters, in-situ monitoring of load and displacement and automatic calculations of both instrumented hardness and Young's modulus,
- instrumented dynamic Young's modulus tests with spherical, Berkovich, and other indenters, in-situ monitoring of tip frequency changes during surface scanning, and both calculations and maps of Young's modulus,
- micro-scratch-hardness tests per the ASTM G171-03 (loads from centi-N to hecto-N, sliding distances from a few microns to many millimeters) with numerous indenters (spherical, conical, micro-blades, etc.), under a constant load or any other loading profile with capability of simultaneous monitoring of friction, acoustic emission, electrical resistance, etc.
- nano-scratch-hardness tests per the ASTM G171-03 (loads from 0.1 micro-N to hecto-N, sliding distances from 1 to 100 microns) with numerous indenters (Berkovich, spherical, etc.) and AFM-like imaging of scratches with the same tip.

The UNMT-1 allows for multi-scale measurements of the same sample without its removal, just with an easy exchange of the mentioned indentation and scratch modules.

4 Results and Discussion

The evaluation results of mechanical and tribological properties of numerous specimens in ambient conditions are summarized in Table 1. Whereas the "+" shows that the technique was sufficient to measure the property of the sample, the "-" indicates that the technique failed to evaluate the film properties without the substrate effect.

Micro-indentation

Instrumented indentation tests were performed on bulk metal specimens with a Rockwell diamond indenter with tip radius of 200 micron. The maximum loads for aluminum, brass, and steel specimens were about 30, 70 and 150 N, respectively. Figure 2 shows the representative load-displacement plots, the unloading portions of which were analyzed using the Oliver-Pharr methodology [4]. Table 2 presents the mean hardness and Young's modulus values, obtained from 20 tests on each specimen. It also shows the average value of 20 hardness data obtained from traditional Vickers hardness test on the same samples. The average results of the instrumented and traditional techniques were practically the same (the 10-time difference is due to the

Vickers scale), while the deviation in hardness values were found to be less in instrumented indentation compared to the traditional Vickers hardness test.

Table 1: Summary of various tests performed using UNMT-1

Specimens	Micro-indentation		Instrumented		
	Traditional	Instrumented	Micro-scratch	Nano-indentation	Nano-scratch
Bulk Materials	+	+	+	+	+
20μm metallic film	-	+	+	+	+
2μm metallic film	-	-	+	+	+
4 nm DLC film	-	-	-	-	+

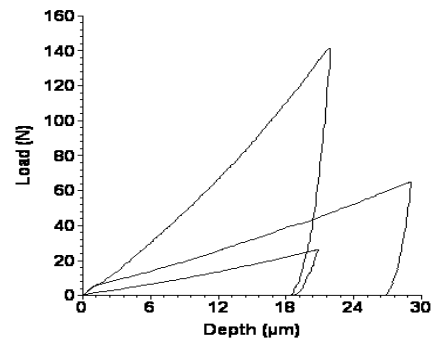


Figure 2: Load-displacement plots for metals

Table 2: Hardness and modulus data for aluminum, brass and steel specimens

Specimen	Hardness (H), MPa	Young's Modulus (E), GPa	Vickers hardness
Aluminum	968±23	74±2	97±11
Brass	2004±19	127±2	201±9
Steel	5202±47	195±8	519±20

Micro-Scratch

The instrumented micro-scratch tests included sliding scratching over 5 mm length at a scratching speed of 0.2 mm/s under a constant load, using a Rockwell diamond indenter. The same tests were done on test specimens and a reference material, usually fused silica which hardness of 9.5 GPa. The scratching loads for the test specimen (F_S) and the reference sample (F_R) should be such that the scratch width dimension on these materials should be similar. The scratch hardness of the specimen (HS) is calculated from the following relation:

$$HS = H_R \cdot \frac{F_S}{F_R} \left(\frac{W_R}{W_S} \right)^2 \quad (1)$$

H_R is the hardness of the reference material. The terms W_R and W_S denote the scratch width values on the reference specimen and on the test sample, respectively. As an example, Table 3 shows the scratch width and hardness values on the fused silica, bare metallic substrate and coated specimens; the coating exhibited hardness three times higher than the substrate.

Table 3: Scratch hardness data on fused silica, bare and coated specimens

Sample	Load, N	Scratch width, μm						Hardness, GPa
		1	2	3	4	5	Mean	
Reference Fused Silica	0.4	13.57	13.81	13.56	13.96	13.72	13.72	9.5
	0.2	9.96	9.78	9.68	10.23	10.03	9.94	9.5
Coating	0.1	7.74	7.79	7.83	8.23	7.98	7.91	7.5
Substrate	0.1	13.75	13.64	13.65	13.86	14.05	13.79	2.4

Static and Dynamic Nano-indentation

Instrumented nano-indentation was performed in both static and dynamic modes, using the same Berkovich indenter. For example, Figures 3 and 4 show ten load-displacement curves that were obtained from static nano-indentation tests on a fused silica and 2 μm thick polymer coating on Si, respectively. They show excellent repeatability of the nano-indentation data, even in the very low force and displacement ranges (Figure 3a). The static nano-indentation data was analyzed automatically to obtain hardness and Young's modulus values.

Figure 5 presents ten frequency-based approach curves, obtained from dynamic nano-indentation on reference polycarbonate specimen and on 2 μm thick polymer film on Si. Again, one can see excellent data repeatability. The data was then analyzed to obtain Young's modulus values.

Table 4 shows the comparative Young's modulus data obtained from static and dynamic nano-indentation tests on various specimens. Each data are the average of 20 tests that were performed on each specimen in static and dynamic modes. The static nano-indentation showed good data for bulk materials and micron-thick coatings, but a significant substrate effect for nano-coatings. The dynamic nano-indentation showed good data for all the specimens, including for ultra-thin films.

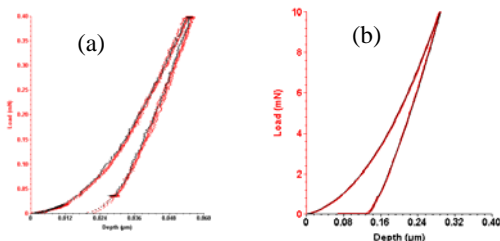


Figure 3: Load-displacement curves obtained from static nanoindentation tests on fused silica up to (a) 0.4 mN and (b) 10 mN

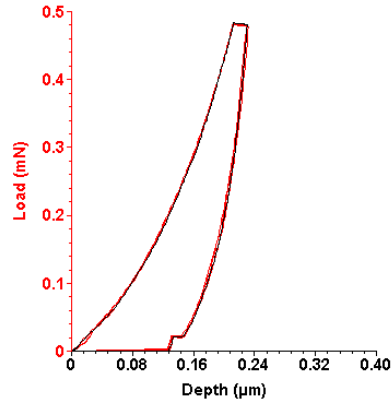


Figure 4: Load-displacement curves from static nano-indentation on 2 μm polymer on Si

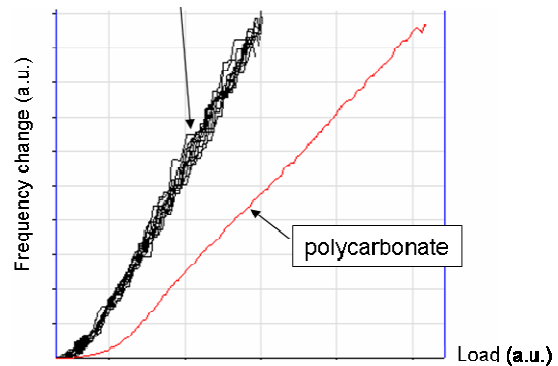


Figure 5: Frequency-approach curves from dynamic nano-indentation

Table 4: Young's modulus data from static and dynamic nano-indentation

Specimens	Young's Modulus, GPa	
	Nano-indenter	Nano-analyzer
Silicon 100	164 \pm 18	164 \pm 14
12 μm polymer on Si	6.85 \pm 0.07	6.0 \pm 0.5
2 μm polymer on Si	7.36 \pm 0.31	6.0 \pm 0.5
2 μm Ti on Si	98 \pm 13	98 \pm 10
2 μm DLC on Si	381 \pm 24	382 \pm 19
1 μm DLC on Si	372 \pm 29	379 \pm 21
100 nm DLC on Si	314 \pm 32*	370 \pm 25
4 nm DLC on Si	195 \pm 39*	361 \pm 27
Reference Polycarbonate	3.62 \pm 0.06	3.50 \pm 0.04
Reference Fused Silica	71.20 \pm 0.65	72.9 \pm 0.8
*Substrate effect		

Nano-Scratch

The Nano-analyzer module of the UNMT-1 was used to measure scratch-hardness by nano-scratching with a Berkovich tip, followed by AFM-like nano-imaging with the same tip. Nano-analyzer software allows for image analysis and measurements to obtain scratch depth profile along any preferred direction of the nano-image of the nano-scratch. The scratch width was then compared to a reference scratch on a material with known hardness. The hardness values were obtained from equation (1) above.

Figure 6 shows an image of a 16 μm x 16 μm surface area after nano-scratching with 500, 200 and 100 μN (left to right) loads on 12 μm polymer coating on Si. The scratch depth profiles along the XX direction of Figure 6 are shown in Figure 7.

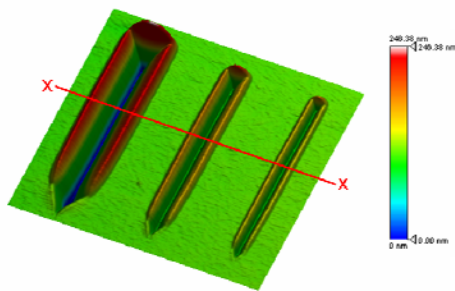


Figure 6: Nano-image of 3 nano-scratches at 500, 200 and 100 μN (left to right) using Nano-analyzer

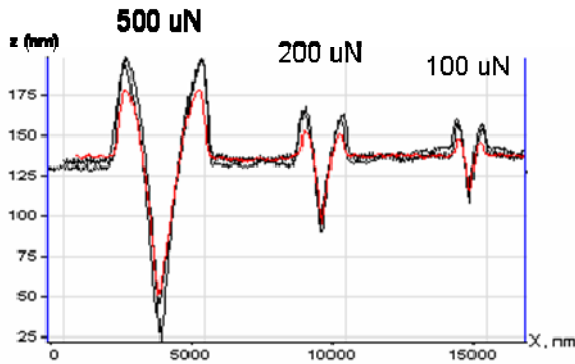


Figure 7: Three repeated scratch depth profiles of 3 scratches along XX in Fig. 6

Table 5 shows hardness data that were obtained in 20 nano-indentation tests vs. 20 nano-scratch tests. The nano-indentation showed good data for micro-coatings, but a substrate effect for nano-coatings. Such substrate effect was absent in the nano-scratch tests. Indeed, a stress distribution in the front of a moving indenter, penetrating into the tested material by several times more than the indenter size, extends into the substrate during nano-indentation, but stay within the nano-coating in the nano-scratch mode.

Table 5: Nanoindentation and Nano-scratch hardness data using UNMT-1

Specimens	Hardness, GPa	
	Nano-Indenter	Nano-Analyzer
Silicon 100	11.4±1.8	11.6±1.0
12 μm polymer on Si	0.29±0.01	0.27±0.03
2 μm polymer on Si	0.44±0.01*	0.33±0.04
1 μm DLC on Si	30.5±2.9	31.2±1.7
100 nm DLC on Si	24.6±3.6*	30.8±1.7
4 nm DLC on Si	15.7±3.2*	29.1±1.9
Reference Polycarbonate	0.23±0.004	0.21±0.03
Reference Fused Silica	9.52±0.07	9.57±0.50
*Substrate effect		

Scratch-Adhesion

UNMT-1 is widely used for evaluation of adhesion and tribological properties of bulk, thin and thick films [2]. One such test mode is scratch adhesion, with a micro-indenter or a micro-blade, performed by sliding under a linearly increasing load (Fz). The failure of the coating is characterized by sudden change in coefficient of friction (COF) or contact acoustic emission (AE). Adhesion strength of the coating or thin film is characterized by the corresponding load at which COF and AE exhibit a sudden change.

Figure 8 shows data from three scratch-adhesion tests using a diamond stylus of 12.5 μm tip radius, at a sliding speed of 0.5 mm/s over a distance of 10 mm on a patterned LCD display with a coating layer sequence of indium-tin-oxide/overcoat/matrix on a glass substrate. At the point of failure at load of about 16 mN, both COF and AE increased. The periodic bumps in the COF and Fz plot were due to the rapid interaction of the diamond tip with the patterned top surface of the specimen. Table 6 shows the COF, AE and scratch-adhesion strength data of the top indium-tin-oxide layer.

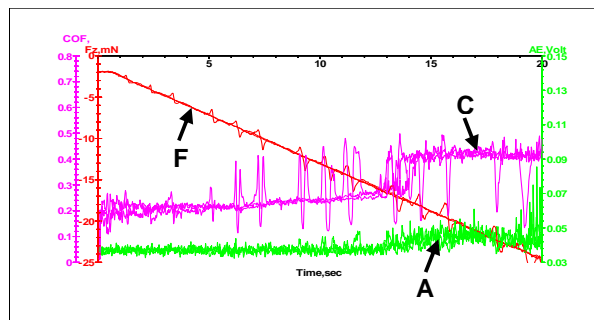


Figure 8: Fz, COF, and AE plots for scratch adhesion tests on LCD specimen.

Table 6: Scratch adhesion test data on LCD specimen

Specimens	Hardness, GPa	
	Nano-Indenter	Nano-Analyzer
Silicon 100	11.4±1.8	11.6±1.0
12 µm polymer on Si	0.29±0.01	0.27±0.03
2 µm polymer on Si	0.44±0.01*	0.33±0.04
1 µm DLC on Si	30.5±2.9	31.2±1.7
100 nm DLC on Si	24.6±3.6*	30.8±1.7
4 nm DLC on Si	15.7±3.2*	29.1±1.9
Reference Polycarbonate	0.23±0.004	0.21±0.03
Reference Fused Silica	9.52±0.07	9.57±0.50
*Substrate effect		

5 Conclusions

In the micro- and nano-indentation tests, the indents under 5-10% of the film thickness have produced repeatable and apparently substrate-independent hardness and Young's modulus results.

In the micro- and nano-scratch tests, the scratches under 30-35% of the film thickness have produced repeatable substrate-independent hardness results.

In the micro-indentation tests, traditional Rockwell and Vickers hardness tests produced more data variability than the instrumented-hardness tests with the same indenters in the same test setup, though the statistics requires more data.

The UNMT-1 provides a unique single platform for comparative studies of mechanical and tribological properties on micro- and nano-levels for thin films, thick coatings and bulk materials.

6 Future Study

In the micro- and nano-indentation tests, the indents Next tests will be focused on indentation and scratch evaluation of coatings at extreme high and low temperatures, using UNMT-1 chamber modules.

7 References

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