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Adhesion testing of atomic layer deposited TiO₂ on glass substrate by the use of embedded SiO₂ microspheres

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Adhesion testing of atomic layer deposited TiO₂ on glass substrate by the use of embedded SiO₂ microspheres

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In this paper, the authors present a new adhesion test method, which is under development, to study the interfacial mechanical parameters of atomic layer deposited (ALD) thin films. A highly sensitive lateral force adhesion testing tool was used to measure the lateral detaching force of 8 μm diameter SiO₂ microspheres embedded in 100 nm ALD TiO₂ thin film grown in 200 °C. The resulting holes in the coating were characterized with scanning electron microscope plus energy dispersive x-ray spectroscopy and the delaminated areas were measured with image analysis software. The corresponding detaching force (F) was compared to the delaminated area (A) to calculate the critical stress value (σ), which relates to the mechanical adhesion of the coating and also includes the effect of other influencing factors such as the film cohesion. The measured critical stress (σ) of the ALD TiO₂ coating on a glass substrate was 36 ± 12 MPa based on the measurement of 43 microspheres.

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I. INTRODUCTION

Ultrathin films down to one atomic layer thickness can be produced by atomic layer deposition (ALD) with high conformality and excellent thickness control.¹ ALD thin films are typically used in silicon-based electronics and microelectromechanical systems industry.^{1–3} Thin film functional characteristics and performance are highly dependent on sufficient adhesion between the film and the substrate.⁴ Conventional adhesion testing methods for thin films include scotch tape testing, scratch-testing, pull-off testing, peel-testing, bend-testing, to name a few.^{4–6} There is no universal technique for determining interfacial toughness. Test-specific factors and residual stress affect the measured adhesion,⁴ and the results of all the different adhesion testing methods are not easily comparable and give qualitative results at best.⁷ Conventional adhesion testing of very thin films in the nanometer range can be problematic; for example, during scratch testing, the substrate can break before the film is delaminated,⁸ and thus new measurement methods are needed to test thinner films. New approaches to study the adhesion behavior of atomic layer deposited thin films include shaft-loading blister testing⁹ and scanning nanowear.⁸ Matoy *et al.* studied interface fracture properties of silicon oxide and metallic thin films by deflecting microcantilevers fabricated by focused ion beam machining¹⁰ that has similar test geometry as our embedded microsphere test structure.

In this paper, we present a new adhesion test method which is under development, where microspheres embedded into an ALD coating are detached and the resulting delaminated area

is compared to the detaching load to define critical stress value related to mechanical adhesion. More specifically, the adhesion of 100 nm ALD TiO₂ thin film to glass substrate is measured by detaching embedded 8 μm SiO₂ microspheres with NanoGalax¹¹ CellAdhesion lateral force testing equipment and defining the delaminated area with scanning electron microscope (SEM) and digital image analysis.

II. EXPERIMENT

SiO₂ microspheres in an ethanol dispersion were deposited and embedded in ALD titania (TiO₂) thin film on a glass substrate. The spheres were detached with NanoGalax CellAdhesion testing equipment [Fig. 1(a)] with a custom micromachined tip having a tungsten wire glued to it [schematic presentation in Fig. 1(b)] to accurately target individual microspheres. The resulting holes in the coating were characterized with SEM, and the delaminated areas were measured with ImageJ digital image analysis software.¹²

A. Sample fabrication

SiO₂ microspheres with the vendor specified average diameter of 8 μm (with a coefficient of variation <10%) purchased from Cospheric LLC were dispersed and ultrasonicated in ethanol to create a 0.005% w/v solution with a good dispersion. A droplet of the dispersion was deposited and dried on a glass substrate (Menzel-Gläser microscope slides with 72.2% SiO₂, 14.3% Na₂O, 6.4% CaO, 4.3% MgO, 1.2% K₂O, 1.2% Al₂O₃, 0.3% SO₃, and 0.03% of Fe₂O₃).

The microspheres were embedded in 100 nm ALD TiO₂ deposited at 200 ± 5 °C from TiCl₄ and H₂O precursors using Beneq-TFS500 reactor at Micronova Nanofabrication Center of Aalto University. The following deposition cycles

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FIG. 1. (Color online) (a) Lateral force adhesion testing tool. (b) Schematic presentation of the measurement tip. The micromachined tip has a 15 μm tungsten wire attached at the end of the tip that is used to accurately detach individual spheres while measuring the lateral force required for detachment.

were used: TiCl₄ pulse and purge (waiting time 200 ms, pulse 300 ms, waiting time 500 ms, and purge 1.5 s), H₂O pulse and purge (waiting time 200 ms, pulse 240 ms, waiting time 700 ms, and purge 1.5 s) with a deposition rate of 0.425 Å/cycle. The final structure of the embedded spheres in the coating can be seen in Figs. 2 and 3(a).

B. Measurement with lateral force adhesion tester

Adhesion measurement was carried out by detaching the embedded microspheres using NanoGalax CellAdhesion

FIG. 2. Optical microscope view of the measurement. The tungsten wire attached to the tip can be seen in the lower left corner.

FIG. 3. (a) Microsphere before measurement. (b) The resulting hole after measurement. SEM image is tilted 45°.

lateral force adhesion tester [Fig. 1(a)] with a custom micro-machined tip having a 15 μm tungsten wire glued to the end of the tip. The tip module was calibrated before the measurement with proprietary NanoGalax methods. In Fig. 2 is a view of the optical microscope measurement including the tungsten wire attached to the tip on the lower left corner.

The critical stress σ (MPa) was defined as the detachment force F (μN) divided by the delaminated area A (μm^2).

C. Characterization with SEM + EDS and digital image analysis

The sample was characterized with Hitachi 4700 FE-SEM before [Fig. 3(a)] and after [Fig. 3(b)] the lateral force measurement. Forty-three microspheres were identified and their coordinates were recorded to find each individual sphere before and after the measurement. Energy dispersive x-ray spectroscopy (EDS) was used to confirm delamination of the coating by comparing the elements found in the hole and in the coating. The delaminated area of the resulting hole was masked with Adobe Photoshop, and the area was measured with ImageJ digital image analysis software.

III. RESULTS AND DISCUSSION

A. EDS analysis

Besides visual observation in SEM, EDS analysis was used to confirm coating delamination (Fig. 4), and the results can be found in Table I. EDS analysis from the film area (spectrum 1

FIG. 4. (Color online) EDS analysis was done to confirm delamination of the ALD titania coating. Spectrum 1 is from the film area. Spectrums 2 and 3 are from the delaminated area.

in Fig. 4 and Table I) resulted in a Titanium signal of 13 wt. %, whereas EDS analysis from the hole area (spectrums 2 and 3 in Fig. 4 and Table I) resulted in no titanium signal at all, confirming that the film had been delaminated.

B. SEM characterization for area calculation and digital image analysis

After the SEM characterization three main mechanisms were observed that consume energy during the detaching of the spheres: film–substrate interfacial failure [Fig. 5(a)], film–sphere interfacial failure [Fig. 5(b)], and cohesive failure (breakage of the film that can be seen as the edges of the hole in the coating in Fig. 5).

For each microsphere, the area of each specific mechanism was calculated by masking the specific areas with Adobe Photoshop and calculating the masked areas by ImageJ digital image analysis software. One of the masking results is shown in Figs. 6(a)–6(d), where Fig. 6(a) shows the original SEM image, Fig. 6(b) shows the area of film–substrate interfacial failure, Fig. 6(c) shows the area of film–sphere interfacial failure, and Fig. 6(d) shows the area of cohesive failure (breakage of the film).

C. Critical stress measurement results

The samples were divided into three groups according to the major failure mechanism: In group 1, the delamination occurred mostly from the film–substrate interface seen in Fig. 5(a), in group 2 delamination occurred mostly from the

TABLE I. EDS analysis results (in wt. %) from the film area (spectrum 1) and from the hole area (spectrums 2 and 3). Comparison of Ti signal between the film area (13 wt. %) and the hole area (no signal) confirmed that the film had been delaminated.

Spectrum	O	Na	Mg	Al	Si	K	Ca	Ti	Total
Spectrum 1	44.32	5.3	1.89	0.43	31.18		3.51	13.37	100
Spectrum 2	44.56	7.25	2.16	0.52	40	0.51	5.01		100
Spectrum 3	45.82	5.83	2.23	0.57	40.69		4.86		100

FIG. 5. (a) Film–substrate interfacial failure (delamination). (b) Film–sphere interfacial failure. Cohesive failure (breakage of the film) can be observed at the edge of the hole in the coating.

film–sphere interface seen in Fig. 5(b), and in group 3, the delamination occurred from both interfaces (having mixed modes of interfacial failure with no clear dominating failure mechanism). The critical stress measurement results from detaching the spheres for each group can be found in Table II. The critical stress values (σ) are plotted for all

FIG. 6. Definition of different areas for each failure mechanism with digital image analysis. (a) Original SEM image. (b) Masked area for film–substrate delamination area calculation. (c) Masked area for film–sphere delamination area calculation. (d) Masked area for cohesive failure area calculation. The total area of delamination is the combined area of (b)–(d).

TABLE II. Average measurement results for sphere detaching load, delaminated area, and subsequent critical stress σ . In group 1, the delamination occurred mostly from the film–substrate interface, in group 2 the delamination occurred mostly from the film–sphere interface, and in group 3, the delamination occurred from both interfaces $A_{\text{total_del}}$ is the total area of delamination.

Group	Calibrated load (μN)	$A_{\text{total_del}}$ (μm^2)	$\sigma_{\text{total_del}}$ (MPa)
1	391 ± 63	12.6 ± 4.0	33 ± 11
2	385 ± 128	10.0 ± 2.3	39 ± 12
3	372 ± 130	10.6 ± 3.2	37 ± 14
average	383 ± 107	11.1 ± 3.2	36 ± 12

groups in Fig. 7, and the average critical stress of all groups was 36 ± 12 MPa.

The interfacial material pair is essentially similar for groups 1–3 (TiO₂–SiO₂) explaining why the values in Fig. 7 are in the same range. Puurunen *et al.* studied the adhesion of TiO₂ to SiO₂,¹³ but they used significantly thinner films of about 10 nm and annealing up to 1100 °C resulting in noncontinuous Ti-containing layers. The resulting TiO₂–SiO₂–adhesion measured with pull test was 23 MPa, which is a bit lower but within the variation compared to our results (36 ± 12 MPa). For plasma-activated samples annealed at 200 °C, the resulting pull strength was in the range of 8 MPa, but again the film thickness was about 10% of our film thickness. Our results include the effect of film cohesion, so the critical stress value of pure adhesion is even lower than 36 ± 12 MPa.

All groups are within variation limits with each other, but the variation is quite large. The critical stress variation in this work can be caused by possible contamination during the wet deposition of the spheres, where possible impurities accumulate to the base of the sphere during drying due to capillary forces and surface tension. Possible impurities between the ALD coating and the sphere may also explain why some of the spheres were detached from the film–sphere interface (group 2) whereas spheres with possibly less impurities were detached from the film–substrate interface (group 1). Dry deposition of the microspheres will be used

Fig. 7. (Color online) Measured critical stress values σ related to mechanical adhesion (MPa) of the coating. Group 1: delamination mostly from film–substrate interface, Group 2: delamination mostly from film–sphere interface, Group 3: mixed modes of delamination.

for future experiments to avoid possible contamination related to wet deposition.

Besides the adhesion strength of the ALD-film to the substrate and to the microspheres, there are many other influencing factors to the critical stress value such as film cohesion, film stresses (multiaxial state of stress during the detaching of the microspheres), sphere–substrate interaction, and strength of the microspheres, which can have an effect on the measurement results, and the separation of the influence and significance of all the different factors can be challenging. Although the system is a lot more complex, in this work, the most significant factors were estimated to be the film–substrate adhesion strength, the film–sphere adhesion strength, and the cohesive strength of the film. Other factors such as the sphere–substrate interaction and the strength of the microsphere were not considered so significant in this analysis. The adhesion of loose particles on the surface was found negligible and the microsphere material (silica) was chosen to match the strength and mechanical properties of the substrate and under no circumstances did the spheres break during the measurements.

Initial proof-of-concept measurements were done with 1 μm diameter SiO₂ microspheres embedded in 100 nm ALD Al₂O₃ resulting in an average critical stress of 720 ± 390 MPa, but the results are not so reliable. Besides the different coating material, the test geometry was also different because smaller microspheres were used, and the coating thickness to sphere diameter ratio was 1:10, whereas in the experiments conducted in this paper, the coating thickness to sphere diameter ratio was 1:80. Also, in the initial tests, the detaching forces and delaminated areas were not sphere specific but averages of about ten measurements. It became evident that the sphere size of 1 μm was too small for a practical measurement with the optical microscope, and it is possible that the 15 μm wide tip was in contact with several spheres during one measurement explaining the significantly higher critical stress value. To overcome the limitations of the optical microscope, bigger microspheres were chosen for these more thorough experiments presented in this paper.

Other limitations of the measurement method include that the microsphere deposition must be done before the film deposition. Also the mechanical strength of the tungsten wire in the testing tool tip limits the applicable load, so a thicker wire must be used if thicker or more durable films are tested. Also, for the microscope setup, the substrate needs to be transparent, and the next generation device will have microscopes on the side, enabling the use of opaque substrate materials such as silicon.

This is the first demonstration of a new adhesion evaluation method that is especially useful for comparing the adhesion of different ALD-films. The goal is to develop a measurement method for an absolute value of the adhesion strength, but more experiments with different variables are needed to achieve this goal.

IV. SUMMARY AND CONCLUSIONS

Adhesion is a critical factor defining the usability and performance of thin films. Adhesion measurement of very thin

films can be challenging, and thus, there is a need for developing new measurement methods. Often thin film adhesion is said to be good or bad based on the Scotch tape test, but no measurable numbers are given. In this paper, we demonstrate a new adhesion test method especially for ALD thin films measuring the critical stress to delaminate the film including the effect of film cohesion. Three main failure mechanisms were observed, and analysis was made based on the major failure mechanism. Group 1 events represent closely the adhesion behavior of the film and the substrate, and the average critical stress value of TiO₂ on a glass substrate was 33 ± 11 MPa, which was in the same region and within the variation limits of all the groups (36 ± 12 MPa). To further develop the new method and get more comparative results, the next steps include the testing of different film materials, different film thicknesses, depositions done at different temperatures, and the use of different substrates.

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