Vapor Deposited Nanolaminates

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ABSTRACT

We present the latest developments in nanocoatings deposition technology, realized using Molecular Vapor Deposition (MVD®) method. Multi-layer nanolaminates of metal oxides (alumina, titania, silicon oxide, …etc.) and self-assembled monolayers (SAMs) sequentially deposited using an automated system in-situ without breaking a vacuum between layers show improved lifetime and environmental stability (mechanical impact, immersion in liquids, …etc.) compared to just SAM layer alone. We have found that different metal oxides are preferable as an adhesion layers to various materials and as seed layers for organic coatings deposition, thus previously implemented dual layers should be complemented with additional intermediate layer. We show results of trilayer MVD nanolaminates improvement in thermal and catalytic stability, discuss recently developed novel MEMS lubrication schemes, and promising results in moisture barrier applications.

Keywords: MVD, molecular vapor deposition, metal oxides, organic films, nano-laminates, adhesion layers

1. INTRODUCTION

MVD® surface engineering has already proved to be enabling technique for MEMS yield and lifetime improvement, Inkjet nozzles passivation, molds pre-treatment for nanoimprint Lithography, and many other applications [1-3]. The most important advantage of this method is its applicability to wide variety of substrate materials. Lack of bonding sites in non-oxide-based material surfaces, like polymers and some metals, is compensated with “artificial” oxide surface, which is grown in-situ from a vapor phase. Such an adhesion layers are based on metal-oxides, which can be bound with most materials using non-covalent-type linkage. For example, alumina have an ability to incorporate into polymer pores and thus create quite strong bond with the surface. At the same time, we have found that metal-oxide which forms strong bond with substrate material is not the best (or the most stable) surface for functional organic coating. Another intermediate layer is necessary to create strong adhesion and provide maximum density of functional coatings.

2. EXPERIMENTAL

Alumina, titania, and heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (FDTS) coatings were vapor deposited from liquid precursors (obtained from Gelest Inc. and Sigma) using the MVD100 vapor deposition system manufactured by Applied MicroStructures, Inc. Surface cleaning and hydroxylation of the substrates were performed in-situ using a remote RF oxygen plasma source. The metal oxide adhesion layers and FDTS films were grown sequentially at temperatures between 50-80ºC without exposure of the substrate to ambient conditions during the cycling process. Water contact angles were taken using a Rame-Hart Goniometer. Water vapor transmission rate (WVTR) is measured using MOCON Permatran 3/33 water permeation measurement tool at 37 C. and 85% RH.

3. RESULTS AND DISCUSSION

Fig 1. represents a simple nanolaminate comprised of 2 layers, the first- adhesion metal-oxide layer, and, the second – functional Self-assembled monolayer (SAM). Total thickness of this nanolaminate can be adjusted by controlling thickness of metal-oxide within a practical range of 50-500 A. We were able to apply SAM to many polymers, metals, semiconductors and glasses using this scheme. Recently we found that stability of this coating can be further improved by addition of another coating (intermediate) between metal-oxide and SAM.
Fig. 1: Schematics of dual-layer of metal-oxide and SAM

Fig. 2 demonstrates advantages of such 3-layer stack (especially for A1/B1/F1 materials) for thermal stability on Si wafer. Self-assemble coating F1 degrades quite rapidly with temperature; adhesion layer A1 helps with stability, especially up to 250°C; different tri-layer schemes allow to extend usability of MVD coatings up to 500°C.

Fig. 2 Temperature stability for single, double and triple-layer stacks on Si

This approach has also allowed forming quite durable hydrophobic layer on Ni material, as shown on Fig. 3. Triple-layer approach gives performance on Ni similar to Si material.

Fig. 3 Triple-layer stacks temperature stability on Si and Ni

Triple-layers also provide good catalytic stability. Fig. 4 and 5 demonstrate performance of dual and triple coatings deposited on Si and SU8 photoresist materials in DI water immersion. Here again, the best stability is achieved with triple-layer configuration.

Fig. 4 DI water immersion stability of double and triple-layer stacks deposited on Si

Similar stability improvement has been obtained on polymer materials. For example, Fig. 5 represents immersion stability of dual and triple-layers deposited on SU8 photoresist material.

Fig. 5 DI water immersion stability of double and triple-layer stacks deposited on SU8 polymer

Recently we have discovered that nanolaminates deposited using MVD technology can provide quite impressive moisture permeation properties. Fig. 6 shows results of moisture transmission rate measurements on Polyethylene naphtalite (PEN) film (5 mil) with and without MVD alumina coating. We observed 3 orders of magnitude drop in WVTR for <50 Å thick coating deposited on both sides of the film. We plan to continue this development and complement MBD alumina with one or number of organic MVD coatings to improve WVTR beyond $10^{-3}$ g/m2*day region.
Another interesting application of MVD nanolaminates are wear resistant lubrication coatings for MEMS and release coatings for Nanoimprint Lithography. The test structures, based on a double comb drive design, were fabricated in the Sandia SUMMiT V process. Their operation has been extensively discussed in the literature [4]. Briefly, one set of combs is used to apply a static load on a beam, which is pulled against a fixed post; the other set is used for tangential actuation to rub the beam against the fixed post (Fig. 1).

Fig. 7 represents a polysilicon wear test structure we used for testing this coating performance. (crossing beams only; the driving combs are outside of the field of view). The fixed post is shown blown up in the inset for clarity. Apparent contact pressure was about 80 MPa, sliding frequency – 3 Hz.

The results of this tests are presented on.

The carbon-doped alumina coatings were applied to the released microstructures in an MVD100 system by molecular vapor deposition, a technique similar to atomic layer deposition. Trimethylaluminum and water were used as precursors and nitrogen as the purge gas. The chamber temperature was kept below 100°C. A multi-layer process resulted in an alumina coating, 5.8 nm thin and a very smooth surface.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Cycles-to-Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native oxide</td>
<td>$8 \times 10^3$</td>
</tr>
<tr>
<td>Vapor SAM</td>
<td>$4 \times 10^7$</td>
</tr>
<tr>
<td>SiC LPCVD</td>
<td>Testing halted after $10^6$</td>
</tr>
<tr>
<td>Alumina MVD®</td>
<td>Testing halted after $2 \times 10^7$</td>
</tr>
</tbody>
</table>

Table 1. Lifetime of various coatings

We have performed wear tests by applying a tangential actuation voltage (sine wave plus DC offset, 80 V peak-to-peak, 3 Hz). An 80 V DC load was applied to the load actuator, corresponding to a mean contact pressure of 80 MPa. Device failure (i.e., the inability of the tangential actuation voltage to slide the beam across the fixed post, with the static load applied) usually occurs within a few thousand cycles of operations for uncoated devices [3] (Table I). In contrast, the microstructures coated with carbon-doped alumina have so far undergone testing without failure for over $7 \times 10^6$ cycles. This is approximately seven times longer than the SiC-coated structures tested in a similar way.

**SUMMARY**

We demonstrated enhancement of MVD® deposition technology using multi-layer nanolamine schemes. Triple layers nanolaminates, combined from different types of metal-oxides and organic self-assembled monolayers provide higher thermal and immersion stability. MVD metal oxides also show very impressive performance as lubrication coatings for MEMS and Nanoimprint Lithography. Nanolaminates deposited by MVD technique hold a good promise for moisture barrier applications.

**REFERENCES**