Low Temperature Nanolayers Of Metal Oxides By MVD^{TM}

B. Kobrin, N. Dangaria, J. Chinn
Applied Microstructures, Inc.
1020 Rincon Circle, San Jose, CA 95131 USA
Tel: 1-(408) 907-2885; Fax: 1-(408) 907-2886
e-mail: boris_kobrin@appliedmst.com

ABSTRACT

Highly conformal layers of alumina (Al_2O_3) and titania (TiO_2) have been deposited on a variety of substrate materials using Molecular Vapor Deposition (MVD^{TM}). These metal oxide coatings function as excellent adhesion promoters for the attachment of subsequent functional organic layers. Physical properties of these films including roughness, thickness, and refractive index data are presented. Properties of nano-laminates consisting of alternating metal oxide/ organic layers are also described.

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

1. INTRODUCTION

Molecular Vapor Deposition (MVD^{TM}) techniques and equipment have been successfully used for many coating applications in the MEMS, disk drive, and nano-imprint lithography fields [1,2]. By exploiting the ability of MVD to deposit an in-situ metal oxide "adhesion layer," functional organic layers (hydrophobic, hydrophilic, reactive, …etc.) can be attached to a variety of different substrate materials. MVD allows for the creation of high quality metal oxide adhesion layers on substrates at low temperatures. This allows for functional coatings to be applied on plastics, polymers, fibers, and other materials that can't tolerate high temperatures. Metal oxides are desirable because they have better mechanical and dielectric properties than organo-silanes. Moreover, the refractive indexes of thin vapor deposited metal oxide films can be tuned for various optical applications.

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 MVD^{TM}-100 vapor deposition system manufactured by Applied MicroStructures, Inc. Surface hydroxylation of the substrates was performed *in-situ* using a remote RF oxygen plasma source. The metal oxide adhesion layers and FDTS films were grown sequentially in-situ at temperatures between 35-80ºC without exposure of the substrate to ambient conditions between coating steps.

Water contact angles were taken using a Rame-Hart goniometer. Roughness and texture measurements were obtained using a Veeco Dimension AFM system. TEM samples were prepared by the wedge polishing method (polishing both cross section surfaces to a thickness of a few microns) followed by ion thinning to electron transparency on a Gatan PIPS ion milling system operating at 4kV. Samples were then visualized on a JEOL 2010 TEM at 200kV operating voltage. Thickness and refractive index measurements were made using a Gaertner LSE Stokes Ellipsometer. Hardness data was obtained using a CETR nano-analyzer NA-1 with a Diamond Berkovich tip. Non-destructive (pure elastic) indentations were used for modulus evaluation. Hardness values were obtained from scratch tests with ultra-shallow traces (< 5.5 nm). Tribological properties of the films were determined using MEMS microstructures. Prior to coating, the microstructures were released using sacrificial layer liquid etch followed by supercritical drying. The apparent work of adhesion was evaluated using a cantilever beam array method [3].

3. RESULTS AND DISCUSSION

Thin (1-30 nm), uniform (<5%), and conformal layers of Al_2O_3 and TiO_2 deposited using MVD techniques on semiconductors, metals, and polymer substrates yield very smooth and texture-free films, as shown in Figures 1 and 2.

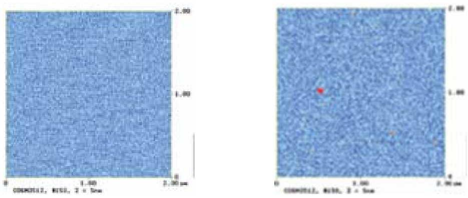

Figure 1: Surface roughness of 7 nm (a) and 28 nm (b) Al_2O_3 film on Si deposited by MVD^{TM}, RMS = 0.1- 0.3 nm

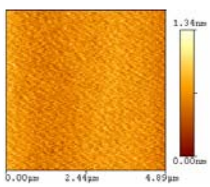

Fig. 2 Surface roughness of 5 nm TiO_2 deposited on Si my MVD^{TM}, RMS = 0.2 nm

Young's modulus hardness data, measured using nano-indentation and scratch resistance methods, presented in Table 1, are in good agreement with the previously published results for vapor deposited Al_2O_3 films [4]:

	Young's modulus	Hardness
Sample	(Gpa)	(Gpa)
AM127	165.9±3.5	12.3+2.5
AM136	163.8±3.3	11.0±1.6

Table 1. Mechanical properties of MVD^{TM}-deposited of Al_2O_3 layers

As shown in Table 2, metal oxide layers as thin as 15-20Å effectively promote adhesion of organic layers to plastic materials. Similar advantages of metal oxide adhesion layers have been obtained on metals and glass.

Material	Initial State	Plasma	Adhesion Layer	Functional (Perfluoro)
Water Contact Angle °C				
Si	27	5	5	114
Polycarbonate	98	5	5	112
PMMA	71	20	5	114
Polystryrene	68	5	5	113
Si	27	→		114
Polycarbonate	98	→		23
PMMA	71	→		52
Polystryrene	68	→		36

Table 2. DI water contact angles measured on various coated plastic materials with and without a metal oxide adhesion layer

The MVD technique has also been used to create nano-laminates by alternating sequential deposition of a metal oxide and a perfluorinated organic compound as shown in Fig. 3. In this example, the DI water contact angle for the initial substrate and after each lamination step is shown along with thickness data for each layer in the laminate structure.

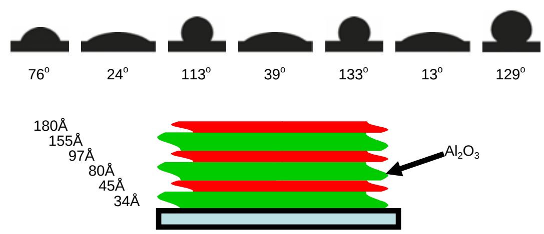

Fig. 3 Nano-laminate of alternating organic and metal oxide layers

The corresponding TEM cross-section image of a 10-layer nano-laminate is shown on Fig. 4.

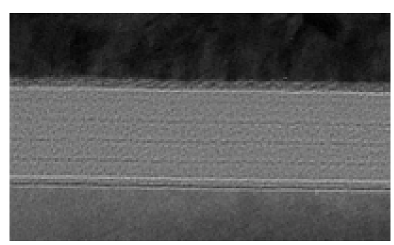

Fig. 4 TEM image of a 10-layer nano-laminate film composed of Al_2O_3 and FDTS

Metal oxide adhesion layers can also be used as adhesion layers for anti-stiction organic coatings on MEMS materials like polysilicon. Figure 5 shows a typical interferogram of cantilever beams coated with MVD^{TM} layers. The Al_2O_3 layer (50 Å thick) and FDTS anti-stiction coatings were both deposited in-situ in an MVD™-100 system. A transition from the free-standing to arc-shaped beams happens at 1550 µm indicating that vapor deposited Al_2O_3 layers were able to penetrate high-aspect-ratio structures and reduce work of adhesion of polysilicon material from >20,000 to below 3 µJ/m^2.

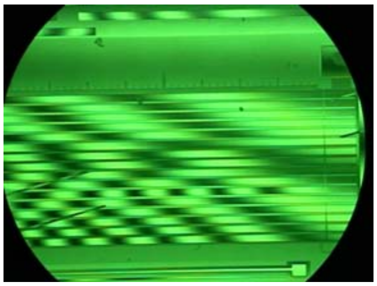

Fig. 5 Interferogram of MVD-coated cantilever beams after actuation.

The use of different metal oxide and silicon oxide coatings has also been shown to allow for the tuning of refractive indexes. As shown in Figure 6, silicon oxides and metal oxides vapor deposited either separately or co-deposited using a mixture of precursors form layers having a wide range of refractive indexes (N = 1.4 - 2.2 at 650 nm).

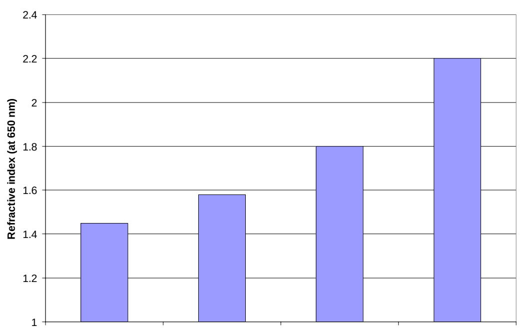

Fig. 6 Refractive index of MVD-deposited metal oxides

SUMMARY

The use of metal oxides films as in-situ adhesion promoters for functional organic coatings has been demonstrated and several advantageous properties of these films (adhesion, mechanical and optical) shown. An example of a nano-laminated film, composed of alternating an Al_2O_3 layer and an FDTS self-assembled monolayer is also described.

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