Reactive Ion Plating - A Novel Deposition Technique for Improved Optical Coatings

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Summary

Reactive Ion Plating Deposition (RIPD) is a plasma-enhanced thermal evaporation (physical vapor deposition, PVD) technique. A high current (50-60 A), low voltage (50 - 80 V) arc produced in a hot filament argon plasma source is burning into the crucible of a modified electron beam evaporator. The arc discharge ionizes the residual gas atmosphere in the coating chamber (O_2 at about 10^{-4} to 10^{-3} mbar) as well as some of the evaporant. This creates an intense plasma in contact with the substrates. The substrates (dielectric optical elements) are mounted on an insulated holder (rotary dome). Because of receiving more electrons out of the plasma than ions, they obtain a negative self-bias of 5 to 50 V. This bias attracts and accelerates the positive ions out of the plasma (oxygen and evaporant species). The electrostatic nature of the attraction causes the accelerated ions impinge normal onto the surface of the substrate and the growing film. The resulting films are very dense, smooth, hard, and adherent to the substrate. They have also higher refractive index and laser-induced damage threshold than comparable oxide films deposited by standard electron beam evaporation. Here we report recent results obtained with single layer TiO_2 and multilayer TiO_2/SiO_2, ZrO_2/SiO_2, and Ta_2O_5 coatings, which illustrate the improvements achieved with RIPD.

Introduction

Thin films, particularly those deposited on solid substrates from a vapor phase, are usually quite different from the respective bulk material as to their structure and properties.[1] For this reason, thin films are sometimes considered the fourth state of matter (if plasma physicists claim plasma being the fourth state, thin film physicists will be content with the fifth state, too). One of the more common deposition techniques for making oxide thin films on foreign substrates is Physical Vapor Deposition (PVD).[2] Because of the specific deposition conditions - condensation from a supersaturated vapor phase at fairly high rates - and the close proximity of surfaces and interfaces most thin films are in non-equilibrium, and special physical and chemical considerations apply.[3]

One key problem coming along with this special situation is the porosity of thin films grown by PVD. Electron microscope investigations of fractured edges of thin films[4] revealed that many metals and most dielectrics form thin films with a columnar microstructure.[5] So-called structure-zone-models relate the apparent microstructure to process parameters during deposition, notably the substrate temperature[6] for thermal evaporation. In addition, gas pressure for sputter processes[7] and bias potential for ion-plating deposition[8] of metals determine the structure of the films. The formation of columns could be satisfactorily explained by hard-disk simulation[9] and by computer simulation[10] employing ballistic aggregation[11] as well as molecular dynamics models.

Recently, low-voltage reactive ion-plating deposition (RIPD)[12] appeared as a versatile method of producing hard thin film coatings with bulk-like properties for a variety of chemical compounds. These include nitrides for metallurgical applications,[13] and oxides for optical coatings.[14,15] Ion-plating deposition of oxide and nitride coatings for optical applications operates at about 100°C. The capability of depositing dense, hard oxide thin or thick films at such a low temperature is advantageous for all applications where the substrate does not allow for the typical temperatures of 300-500°C used with other PVD processes. Therefore, RIPD is fully compatible with most optical materials including glasses with a low softening point. Prospects are excellent[16] that the technique can be modified such that hard, durable coatings will be producable at substrate temperatures below 100°C.

Experimental

The Center for Research in Electro-Optics and Lasers (CREOL) at the University of Central Florida (UCF) in Orlando commissioned a state-of-the-art high vacuum box coater BAP 800 from BALZERS in March 1988. This coating equipment is specifically equipped for reactive ion plating deposition (RIPD).[17]

At pre-acceptance tests conducted at the manufacturer's plant near Balzers, Liechtenstein, this equipment delivered stunning preliminary results. Oxide coatings were deposited onto standard-quality witness samples made from sheet glass. The non-cleanroom environment present at these tests in the assembly hall was inappropriate for achieving optimal results because of likely contamination of the films. The new thin film laboratory at CREOL provides the necessary environment for further improvement. The results reported here were obtained with samples made at the pre-acceptance tests, single layer coatings of TiO_2 in various thicknesses and multilayer interference coatings consisting of TiO_2/SiO_2, ZrO_2/SiO_2, and Ta_2O_5/SiO_2. A view more samples were already made at the new location of the BAP 800 equipment at CREOL.

Dielectric materials are more difficult to deposit using ion plating than metals, particularly on dielectric substrates, because of electrostatic charging effects. However, the process has been developed by BALZERS to give reproducible results in laboratory deposition runs and, to some extent, in pilot production.[18] The metal or a suboxide of the desired oxide is molten in an electron beam evaporator (6-10 kW power) at or below 10^{-6} mbar. After admitting the reactive gas into the coating chamber (at a partial pressure of 10^{-4} to 10^{-3} mbar), a low-voltage, high-current (50-80 V, 50-60 A) plasma arc burns into the melt which acts as the anode.[19] The reactive gas can be oxygen, nitrogen, a mixture of the two, or another gas. A hot filament source delivers the plasma arc which is sustained with Argon at about 2 mbar. A 1 mm diameter orifice serves as a differential pressure stage.

The large electron current flowing from the cathode to the melt produces an argon plasma arc which ionizes the vapor above the source and the reactive gas in the coating chamber. The plasma is in contact with the dielectric substrates which sit on isolated holders. Electrons leaving the plasma more easily than the heavier ions charge the substrates negatively. A self-bias of -5 V to -60 V results which attracts and accelerates the positive ions (vapor, oxygen, argon) from the plasma environment.[20] The impact of ions in this energy range is apparently just right to densify the growing film by a momentum transfer process.[21] Resputtering does not seem to occur except possibly as preferential sputtering from asperities protruding from the surface of the film. This probably helps to smoothen the film surface.

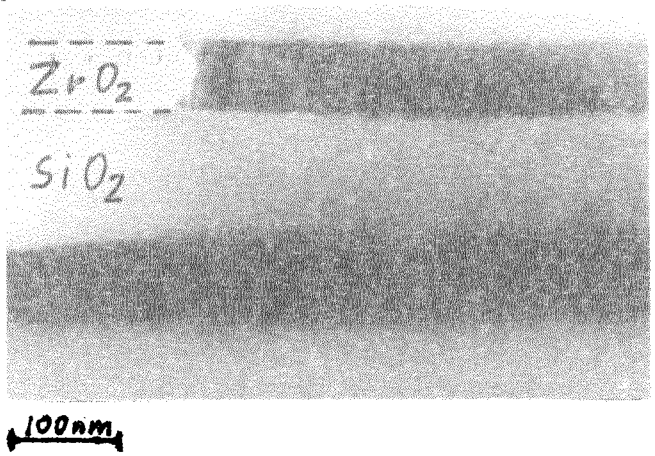
Results

The results of a fairly comprehensive characterization of a number of coating samples are as follows:

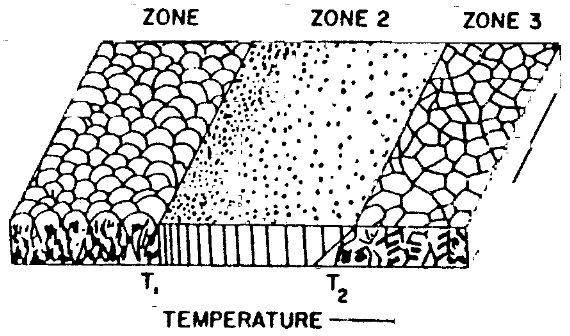
1. Electron micrographs of thin film cross-sections show no observable voids or columnar microstructure for TiO_2 and SiO_2 coatings up to 100,000X magnification, whereas ZrO_2 exhibits a very densely packed polycrystalline texture, with smooth surfaces though, which resembles very closely the Zone III in the classical Structure Zone Model (SZM) by Movchan and Demchishin[6] (Figure 1a, b). Specimen preparation included a replication technique of fractured thin film edges[4] and direct sectioning of the films with a microtome.[22] Figure 2 shows electron micrographs of direct cross-sections of single layer TiO_2 coatings, a) deposited by reactive evaporation (RE) onto a glass substrate heated to about 300°C, b) deposited by reactive ion-plating (RIPD) onto an unheated glass substrate. Although the sectioned specimens are a little too thick to produce clear prints, the following observations can be made:

Feature	RE-coating	RIPD-coating
Adhesion to substrate	poor, delaminated	good, survived sectioning
Texture, microstructure	columnar, filamentary	dense, vitreous
Surface of the films	rough	smooth

Table 1. Qualitative evaluation of direct cross-section TEM micrographs.



1.a.: Direct cross-section TEM micrograph of a ZrO_2/SiO_2 multilayer by RIPD.[2]



	ZONE 1	ZONE 2	ZONE 3
METALS	$<0.3\,T'_m$	$0.3-0.45\,T'_m$	$>0.45\,T'_m$
OXIDES	$<0.26\,T'_m$	$0.26-0.45\,T'_m$	$>0.45\,T'_m$

	T_1 [K]	T_2 [K]	T_m [K]
ZrO_2	648	1273	2973
Al_2O_3	623	1173	2323

Fig. 1.b: Structure Zone Model after Movchan and Demchishin.[6]

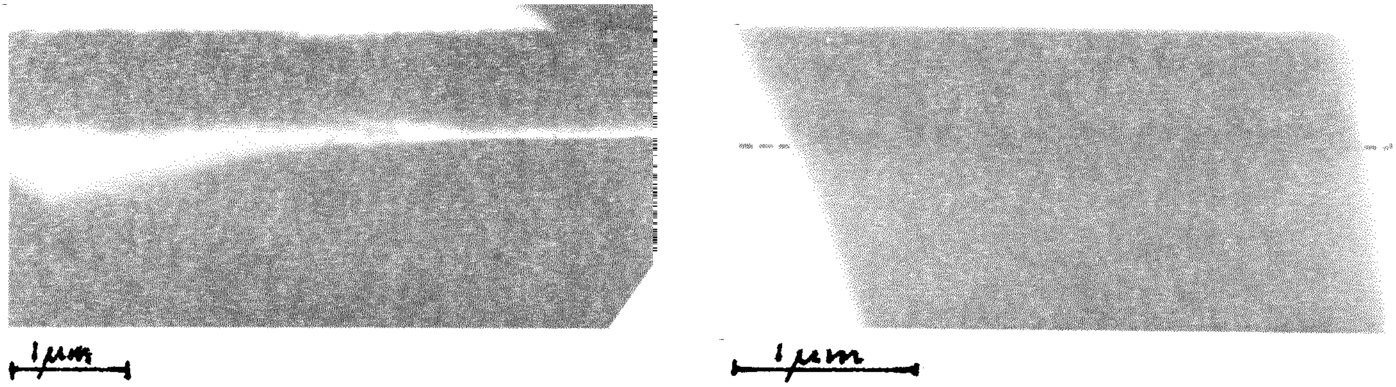
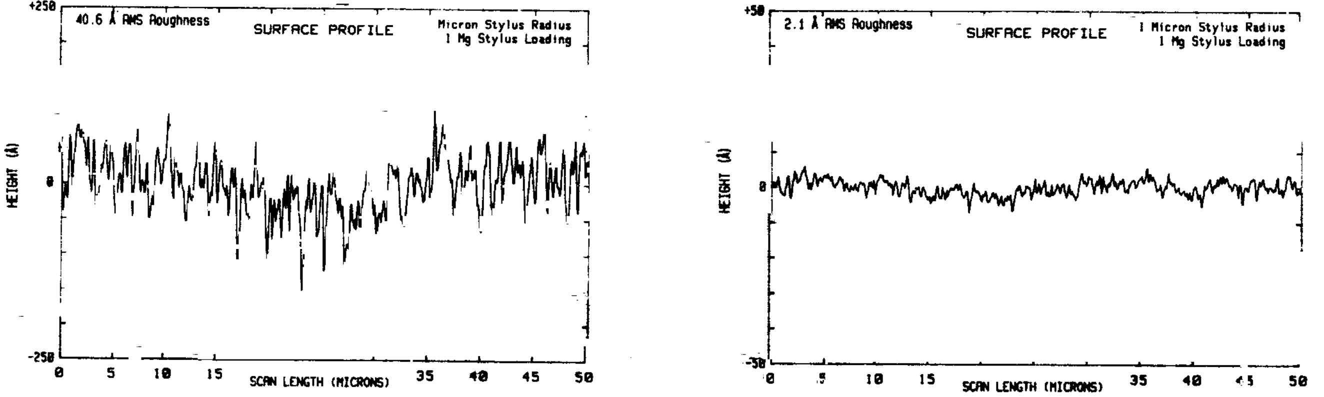


Fig. 2. Direct cross-section TEM micrographs of single layer TiO_2 coatings, made
a. by reactive evaporation b. by reactive ion-plating deposition.

2. Talystep surface profiling[23] (by J. Edgell at the University of Alabama in Huntsville, UAH) of TiO_2 single layer coatings shows that the films are very smooth indeed. Their roughness is about 0.2-0.3 nm rms for up to 500 nm physical thickness, with little variation over the whole thickness range. This compares with 4-5 nm rms roughness for similar films deposited by standard reactive evaporation (Fig. 3a,b).



3. Talystep surface profiles for half-micron thick TiO_2 single layers made by
a.) reactive evaporation b.) reactive ion-plating deposition

3. Investigations with a Raman microprobe (by Prof. Boon Loo and his students at UAH) revealed no crystalline microstructure for ion plated TiO_2 and ZrO_2 coatings. In contrast, the Raman spectra of TiO_2 single layers of comparable thickness deposited by reactive evaporation show a pronounced Anatas signature[24] (Fig. 4a,b).

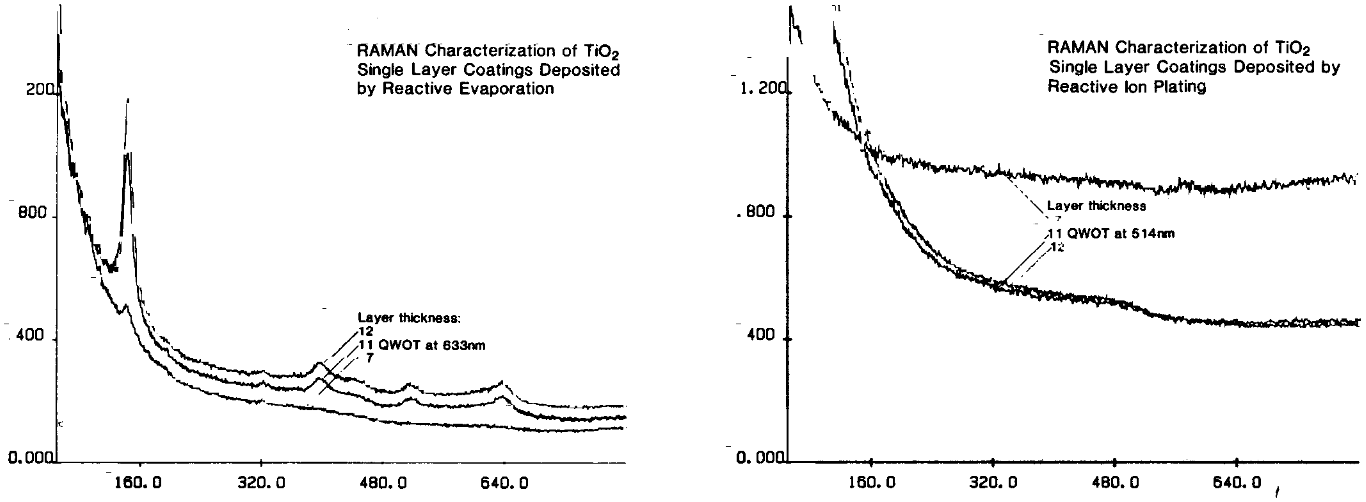


Fig. 4. Raman spectra obtained from about half-micron thick TiO_2 single layers, a.) by reactive evaporation b.) by reactive ion-plating

4. The-laser-induced damage threshold[25] (LIDT) of some coatings was measured by Montana Laser Optics (Dr. Steve Seitel and Mark T. Babb) for 13 ns pulses with 10 Hz repetition frequency, 1 mm spot diameter, at 532 nm wavelength. Single layer TiO_2 coatings made by RIPD had about 2 times higher LIDTs than those made by conventional reactive evaporation (Table 2). ZrO_2 seems to add another factor of 2 in LIDT enhancement.

Quarter Wave Optical Thickness (QWOT)*	LIDT [Jcm^{-2}] A React. Evaporation	B React. Ion-Plating
1	0.61	1.30
3	----	0.98
7	0.44	0.61
11	0.32	0.73
12	0.32	0.71
For comparison: ZrO_2		
11	----	1.30

*QWOT = 633 nm for A, 514 nm for B

Table 2. Laser-induced Damage Thresholds (LIDT) of single layer TiO_2 coatings

5. The mechanical properties of ion-plated oxide coatings, investigated earlier by researchers at BALZERS, are improved hardness and adhesion over that of conventionally deposited coatings.[26] Table 3 summarizes these results.

Feature	RE-coating	RIPD-coating
Knoop indentation hardness tests	Microhardness decreases with film thickness	Microhardness increases with film thickness, to the bulk value of Rutile
Adhesion tests (LSRH scratch test[28])	1.7 kg lbc[27] slight cracking of the glass substrate	2.2 kg lbc[27] onset of strong glass damage
Substrate Temp.	ca. 350°C	ca. 120°C

Table 3: Summary of mechanical properties of TiO_2 thin films.[26]

Discussion

Many of the novel deposition techniques investigated in various laboratories for possible improvements of coating properties are still in a laboratory stage, using home-built equipment or equipment assembled from various components. The coating equipment which we are using at CREOL/UCF for fundamental research as well as exploratory development of RIPD is a full-sized industrial-type 32" box coater of latest technology with micro-computer based process control. Its two electron beam guns can operate with or without the plasma source, thus enabling a direct comparison of the properties of thin films deposited by standard electron beam evaporation and by reactive ion plating deposition. The size and type of the equipment lend it to the application of the technique for a variety of substrates up to 30" diameter, including oddly shaped ones, for uniform coating. Prospective applications of ion-plating deposition are numerous because of the unique properties of the resulting coatings.

Conclusions

The combination of a strong plasma discharge together with high-rate electron beam evaporation provide for unique properties of the deposition process. These properties include a strong ionization of the evaporant with a consequently high reactivity in the vapor phase and on the coated surface, and the self-biasing of dielectric substrates. This negative self-bias causes positive ions (evaporant) being accelerated onto the surface of the dielectric substrate along field lines which end perpendicularly on the surface. Thus, angle of incidence effects commonly seen in other evaporation (including IAD) and sputter techniques are widely eliminated.

We have presented some results of a comparative study conducted with thin film coatings made by reactive evaporation and reactive ion plating deposition. These results clearly demonstrate significant improvements of RIPD over RE thin films. However, the appreciably larger number of process parameters as compared to standard electron beam evaporation and the numerous applications make necessary the continuing research of the fundamentals of reactive ion plating deposition.

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