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Microstructure Analysis Of Thin-Films Deposited By Reactive Evaporation And By Reactive Ion Plating

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Microstructure analysis of thin films deposited by reactive evaporation and by reactive ion plating

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Electron microscopy, stylus-type surface profilometry, and Raman microprobe characterization show distinct differences between thin films deposited by reactive evaporation and by reactive ion plating. Reactive evaporation yields thin films with the well-known columnar microstructure with appreciable surface roughness and other deficiencies. Low-voltage, high-current reactive ion plating deposition produces thin films which are smooth and dense. Cross-section electron micrographs of ion plated coatings reveal a densely packed polycrystalline structure for ZrO_2 , while TiO_2 appears to form vitreous films. Molecular dynamics computer simulation of the film formation process is in good qualitative agreement with the experiments. The results suggest the expansion of the Movchan-Demchishin structure zone model with an additional zone 4 for the vitreous phase, resulting from superthermal film formation conditions (thermal spiking).

I. 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 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—most thin films are in a nonequilibrium state. For the close proximity of surfaces and interfaces, 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 films⁴ revealed that many metals and most dielectrics form thin films with a columnar microstructure.⁵ So-called structure zone models (SZM's) relate the apparent microstructure to process parameters during deposition, notably the substrate temperature⁶ for thermal evaporation. In addition, gas pressure for sputter processes^{7,8} and bias potential for ion-plating deposition⁹ of metals determine the structure of the films. The formation of columns could be satisfactorily explained by hard-disk simulation¹⁰ and by computer simulation¹¹ employing ballistic aggregation¹² as well as molecular dynamics models.^{13–16}

Recently, ion-plating deposition of optical thin films¹⁷ has become available in the form of low-voltage reactive ion plating^{18,19} as a versatile production method²⁰ for hard, stable coatings with "bulklike" properties. Low-voltage reactive ion-plating deposition (RIPD) of oxides^{21,22} and nitrides²³ operates at about 100–200 °C. The capability of depositing dense, hard thin films at such a low temperature is advantageous for all applications where the substrate does not allow for the typical temperatures of 300 to 500 °C used with other

PVD or "low-temperature" chemical vapor deposition (CVD) processes. Therefore, RIPD is fully compatible with most optical materials including glasses with a low softening point. Prospects are that the process can be modified such that hard, durable coatings will be producible at substrate temperatures below 100 °C, making it suitable for coating of plastics or other temperature sensitive substrates such as nonlinear optical materials.

II. EXPERIMENTS

A. Preparation of sample coatings

In order to compare the influence of the deposition processes of reactive evaporation^{24,25} (RE) and low-voltage reactive ion plating^{21–23} on the microstructure and properties of thin films, we chose TiO_2 single-layer coatings for direct comparison. We included a few all-dielectric multilayer coatings (laser mirrors, edge filters) prepared by RIPD, too. The microstructure of RE multilayer coatings has been investigated previously in extensive studies.^{4,5} Hence, we do not want to elaborate on this part of the subject here. All of the sample coatings investigated in this study were deposited on sheet glass substrates of $50 \times 50 \times 1$ mm, with no particular surface polish.

1. Reactive evaporation

Reactive evaporation of TiO_2 single-layer coatings of various thickness, from one quarter-wave optical thickness (QWOT) to 12 QWOT at 633 nm, was used in a bell-jar coater of the type Balzers BA 510. The starting material, Ti_2O_3 , was evaporated from a tungsten boat at an oxygen partial pressure of $\sim 1 \times 10^{-4}$ mbar. The substrates were heated by radiators located above the rotary dome to a temperature of ~ 300 °C before and during the evaporation pro-

a. Basic configuration (see Fig. 1). The coating equipment Balzers BAK 760/BAP 800 has a box-type high-vacuum chamber approximately 32 in. wide, deep, and high. A 24 in. oil diffusion pump (Balzers BPD 500) with a liquid-nitrogen-cooled baffle assures reaching the residual background pressure of 1×10^{-5} mbar in ~ 30 min, with negligible amount of hydrocarbon contamination as evidenced by residual gas analysis with a quadrupole mass spectrometer. The system is fitted with the Balzers BPU 420 automatic process controller. The film thickness and rate monitor in our coating chamber is of the quartz-crystal type.

TABLE I. Thin films and corresponding starting materials with process parameters for reactive ion plating deposition.

Starting materials	Film deposited	Index of refraction (at 550 nm)	Plasma current (A)	Anode voltage (V)	Deposition rate (nm/s)	Oxygen pressure $\times 10^{-3}$ mbar
Si	SiO ₂	1.49	55	55	0.5	1.1
TiO	TiO ₂	2.45	55	70	0.25	1.5
Ta ₂ O ₅	TaO ₅	2.31	55	65	0.3	0.9
Zr	ZrO ₂	2.27	55	80	0.4	1.3

b. Specific modifications for ion plating (BAP 800).

(i) The BAP 800 employs a low-voltage, high-current plasma source (~ 55 V, 55 A) which is mounted in the lower portion of the door. This plasma source is the core of the reactive ion plating deposition process.

(ii) The two electron beam evaporators, one each of the types Balzers ESQ 110 and ESQ 113, are mounted into the baseplate of the vacuum chamber insulated from ground potential. Also, the single-rotation rotary dome is insulated from ground potential.

c. Process of low-voltage reactive ion plating deposition.

First, the starting material for the thin film (aluminum, silicon, zirconium, titanium oxide, tantalum pentoxide) is molten in one of the two electron beam evaporators. After achieving a uniform melt, an argon plasma discharge burns between the plasma source located in the door of the coating chamber and the crucible (Fig. 1). The crucible of that particular electron beam evaporator, insulated from ground, serves as the anode of the discharge. A low-voltage, high-current power supply delivers 50–60 A at 50–60 V flowing from the hot filament of the plasma source to the crucible of the electron beam evaporator. While the argon in the plasma source chamber (at 2 mbar pressure) is ionized by the temperature of the filament, the electron current ionizes the evaporant above the crucible. Because of the high current flowing through the melt, the starting materials (Table I) need to have some electrical conductivity. This excludes full oxides to be used as starting materials for the deposition of oxide coatings. The apparent exception in Table I, tantalum pentoxide (Ta₂O₅), dissociates easily during the premelting procedure before the ignition of the plasma discharge, gaining sufficient conductivity by becoming more metallic.

The argon plasma created in the hot filament source (at an argon pressure of 2 mbar) is being extracted into the coating chamber, via a 1–2 mm orifice which acts as a differential pressure stage. The partial pressure of the argon in the coating chamber is $\sim 10^{-4}$ mbar during the ion plating process. The substrates to be coated are located above the electron beam evaporators in a rotating dome, which is also insulated from ground potential. This insulation allows dielectric substrates, in particular, but also metallic surfaces like aluminum films and the dome itself, to attain a negative self-bias of -5 to -10 V relative to ground potential, because these surfaces receive more electrons out of the plasma sheath than the less volatile ions. Since the crucible has a positive potential of 50 to 60 V with respect to ground, positive ions (M^+ , MO_x^+) created in its vicinity are attracted to the sub-

strate by the differential potential of -55 to -70 V. Ions generated in the plasma, for instance by an electron transfer process

or also

presumably have a potential difference as low as the negative substrate self-bias with respect to ground (-5 to -10 V). The positively charged ions (argon, oxygen, and evaporant metal and/or suboxides) attracted to the negatively biased substrates follow electrostatic field lines that terminate normal to the surface. Because of this effect, the angle of ion impact on the surface of the substrate and the growing film is normal irrespective of the inclination of the local surface element with respect to the line-of-sight to the evaporation source.

For the reactive ion plating deposition of oxide coatings oxygen was bled into the coating chamber by means of a regulated valve, at partial pressures in the low- 10^{-3} mbar range (see Table I). The reactivity of the ionized and activated oxygen is high enough to allow for the deposition of fully stoichiometric oxides, with metals or suboxides as the starting materials in the electron beam crucible. The ionization and accelerated attraction of an estimated 20% of the starting material and the resulting densification of the growing film allows for the coating of unheated substrates. However, we found it necessary to apply glow discharge cleaning of the substrate surfaces immediately prior to coating them. Because of the power consumption inside the coating chamber during the deposition process (4–6 kW for the electron beam evaporator and ~ 3 kW for the plasma discharge), the substrate temperature rises inevitably during the coating run. Dependent on its duration, the final temperature can be as high as $\sim 200^\circ\text{C}$, for example, when an all-dielectric multilayer reflector (20–24 layers) is being deposited. For single layers and coatings consisting of just a few layers (antireflection coatings, protected aluminum mirrors) we observed a temperature rise to about 80 – 90°C at the end of the coating run.

B. Determination of the refractive index of TiO₂ thin films

From the reflectance spectrum of single-layer calibration coatings of about 5 to 7 QWOT at 550 nm, we determined the refractive index n and the physical thickness t using the

fundamental interference optics relation for reflectance minima or maxima at wavelengths λ_m ,

$$nt = m\lambda_m/4,$$

with m being an integral number. At this time, we did not spend any effort to determine the absorption coefficient or any possibly present gradient of the refractive index.

C. Investigations of the thin-film microstructure

Because of the small physical dimension of thin films in the direction normal to their surfaces (< 100 nm to a few μm thickness), we had to employ high-resolution methods for characterizing their microstructure. The methods of choice, based on our experience and the availability of equipment, were (i) transmission electron microscopy, (ii) Talystep surface profiling, and (iii) Raman microprobe characterization.

1. Transmission electron microscope analysis

For investigations in a transmission electron microscope (TEM), thin films need to be prepared to get specimens of electron transmissible thickness. One method which we applied was replicating the structure of interest, for example, the fractured cross section of a multilayer coating, with a thin carbon film after preshadowing this fracture surface with a mixture of platinum and carbon (Pt-C/C replica technique).⁴ The resolution of the replicas is ~ 2 nm, limited by the size of the clusters which the platinum forms used for the contrast enhancement (preshadowing). The second preparation method was the slicing of tiny chips of the coatings (together with just a bit of the substrate material) embedded in epoxy, with a diamond knife on a microtome.^{26,27} While this technique is widely used in the biological sciences for obtaining electron transparent sections of tissue, it is very difficult to perform with hard and brittle materials such as dielectric coatings and glass. However, we were able to obtain a few useful specimens after a relatively short period of time. Because of the hardness of the coatings, the sections are thicker than would be ideal for electron transmission, with their high density probably hiding some interesting detail. In addition, the figures shown in this paper are likely to have lost some resolution in the reproduction process. The original electron micrographs show more details, which we describe verbally in Sec. III.

2. Surface profiling with a stylus-type instrument (Talystep)

The average roughness of the surface of a substrate or a thin film can be characterized²⁸ by its root-mean-square value δ_{rms} . The measurement can be either optical (noncontacting) or mechanical, with a stylus in contact with the surface. We used the Talystep instrument²⁹ at the optical surface characterization facility established by Dr. Jean Bennett at the University of Alabama in Huntsville (operated by J. Edgell). The stylus used has a radius of $1 \mu\text{m}$; the probing force was 1 mg . The samples were investigated at different sites, with profiles as short as $50 \mu\text{m}$ and up to 2 mm long, the short ones being indicative of the actual film surface, where-

as the long ones typically reflect the influence of the substrate. Despite the "large" stylus radius, the spatial resolution of the surface profiles is better than 100 nm for the surfaces under investigation, because of the very shallow slopes of the roughness features. This particular instrument has a vertical noise level (resolution) of 0.04 nm .³⁰

3. Raman Microprobe

Raman microprobe spectra were taken with an ISA Ramanor U 1000/MOLE Raman microprobe using the 514.5-nm line of an argon-ion laser (Spectra Physics 2020) for excitation. This instrument uses a specially adapted Olympus BH-2 metallurgical microscope to focus the incident laser light onto the sample and to collect the 180° back-scattered radiation. Using this technique, spots as small as $1 \mu\text{m}$ in diameter may be sampled, although the lower limit of the spot size is, in practice, determined by the sensitivity of the sample to thermal damage by the focused laser. Hence, the average spot size in examining the TiO_2 samples averaged from 10 to $100 \mu\text{m}$. The power levels at the sample surface were estimated at $1\text{--}10 \text{ mW}$.

The microscope is equipped with a video camera which allows exact positioning of the laser spot as well as visual examination of the sample before and after sampling. Spectra were taken at different spots on various samples using different objectives and with the incident laser beam defocused to different degrees in order to prevent laser damage to the sample. Mostly, we used the $20\times$ and $50\times$ objectives with the laser beam slightly defocused. The spectral resolution was $3\text{--}5 \text{ cm}^{-1}$.

D. Computer simulation of thin-film growth and microstructure

To simulate the structural evolution of a film where the arriving species are molecules of thermal energy and ions of higher energy, we employed a molecular dynamics (MD) simulation approach.¹⁴⁻¹⁶ Because of the enormous computer time needed to calculate the trajectories of a representative sample of film species, it was necessary to restrict the calculation to a two-dimensional (2D) film representing a

FIG. 2. Basic cell for the molecular dynamics simulation of thin-film growth.

monatomic cross section. Such a calculation will resemble many of the essential features of a full three-dimensional (3D) simulation.

Figure 2 shows the simulation cell where the perfect substrate consists of five atomic layers. The atoms and ions are introduced from the top into the open cell, starting from random positions, traveling at normal incidence towards the substrate. The velocities of atoms located in the lowest substrate layer (row) are periodically reset to zero, simulating a perfect heat sink of zero temperature. For the atom-atom interaction a spherically symmetric Lennard-Jones potential was used. For inert gas ions, the ion-atom interaction was approximated by the purely repulsive Moliere potential.

III. RESULTS

A. Refractive index of TiO_2 thin films deposited by RIPD

Figure 3 shows the refractive index of RIPD TiO_2 thin films in the visible range of the electromagnetic spectrum, in comparison with average values of refractive indices for RE TiO_2 thin films, obtained from the materials file of Macleod's thin-film program.³¹ While the refractive index of TiO_2 thin films deposited by reactive evaporation can vary considerably depending on the process conditions,³² we found the values obtained for several runs of reactive ion plated TiO_2 films remarkably consistent.

B. Transmission electron micrographs of thin-film cross sections

In Fig. 4, we compare the direct cross sections obtained by the microtome technique described above, from single-layer TiO_2 films of ~ 500 -nm physical thickness, deposited by reactive ion plating and by reactive evaporation. The RIPD layer is very dense, with a smooth surface, and an amorphous, vitreous structure (as seen in the original micrograph at the thin edge to the right of the wedged specimen). The RE layer shows a rough surface and a fuzzy, fibrous-columnar structure. The adhesion of this layer to the substrate was apparently insufficient to survive the diamond-knife cutting

FIG. 4. Direct cross sections of single-layer TiO_2 films of ~ 500 -nm physical thickness, deposited by (a) reactive evaporation and (b) reactive ion plating.

process. In Fig. 5, we see at the thin edge (to the left) of the slightly wedged specimen where it is electron transparent randomly oriented, densely packed microcrystallites in the ZrO_2 layer (dark bands). The SiO_2 layers (bright, wider stripes) appear expectedly glassy amorphous. Figure 6 shows the fractured cross-section of a 23-layer all-dielectric multilayer stack ($\text{TiO}_2/\text{SiO}_2$), deposited by reactive ion plating. In contrast to the typical columnar microstructure of conventionally deposited coatings,^{4,5} this coating has the textbooklike appearance of a periodic superstructure consisting of alternating high-index (TiO_2 , bright) and low-

FIG. 3. Dispersion of the refractive index of TiO_2 thin films in the visible, for (a) reactive evaporation (■) (data from Macleod's FILMS program) and (b) reactive ion plating (+).

FIG. 5. Direct cross section of part of a $\text{ZrO}_2/\text{SiO}_2$ multilayer stack.

FIG. 6. Fractured cross section of an all-dielectric multilayer stack (23 layers $\text{TiO}_2/\text{SiO}_2$), deposited by reactive ion plating (Pt-C/C replica).

index (SiO_2 , dark) stratified homogeneous media separated by plane, smooth boundaries.

C. Surface roughness profiles

Figure 7 shows representative surface profiles obtained from the same samples as pictured in Fig. 4. Most remarkably, the rms roughness remained at the very low level of $\delta_{\text{rms}} \approx 0.2$ nm for a whole set of reactive ion plating coated TiO_2 films of various thicknesses, up to ≈ 500 nm of physical thickness, while the roughness of standard TiO_2 single-layer coatings deposited by reactive evaporation expectedly

FIG. 7. Talystep surface profiles (note the different vertical scales) obtained with ≈ 500 -nm-thick TiO_2 coatings deposited by (a) reactive evaporation and (b) reactive ion plating.

FIG. 8. Comparison of Talystep roughness measurements on surfaces of TiO_2 single-layer coatings deposited by reactive evaporation (—) and reactive ion plating (---).

FIG. 9. Raman spectra of TiO_2 single layers of 7, 11, and 12 QWOT, deposited by (a) reactive evaporation and (b) reactive ion plating.

increased with the thickness of the layers (Fig. 8). Although we did not have the opportunity to measure the surface roughness of the sheet glass substrates, we assume it to be at least 1 nm or more based on later measurements of similar uncoated substrates.³³

D. Raman spectra

We subjected the same TiO_2 samples already investigated with the transmission electron microscope (Fig. 4) and the Talystep instrument (Fig. 7) to a Raman microprobe analysis. The resulting Raman spectra (Fig. 9) show distinct peaks of increasing height indicative of the anatase crystalline phase of TiO_2 for reactively evaporated thin films of increasing thickness. The reactive ion plated coatings did not show any peak in the Raman spectrum, indicating the absence of crystalline phases within the detection range of the instrument.³⁴

FIG. 10. Molecular dynamics (MD) simulation (2D) of a Ti film growing under the bombardment of 100-eV Ar^+ ions, in three snapshots.

E. Molecular dynamics computer simulation

Figure 10 shows different snapshots during the ion-surface interaction process. Here a 100-eV Ar ion removes Ti atoms from an overhanging edge, sputters atoms into the void, and at the same time keeps the void open to newly depositing atoms. In this way, fast ion impingement disrupts microvoid formation. The ion-surface interaction process lasts for only ~ 10 ns.

Figure 11 illustrates the difference in the resulting microstructure with and without ion bombardment. The Ti atoms in Fig. 11(a) approach the film surface with thermal energies (0.1 eV) which causes the formation of microcolumns and microvoids. When additional Ar ions (16%) of 50 eV strike the surface, the amount of microvoids is strongly reduced, Fig. 11(b). Because of the repulsive Ar-Ti interaction the probability of Ar incorporation is very small. At best, a tiny amount of Ar is confined in some still existing closed voids. Figure 11(c) shows the result of a MD simulation when Ti^+ ions of 50 eV arrive at the growing film surface, again with an ion-to-atom ratio of 0.16.

The film density depends on the ion energy and the ion-to-atom arrival ratio, j_i/j_A . The density obtained from a number of film growth MD simulations for a Ti film growing under Ar^+ bombardment is shown in Fig. 12. In the case of small ion-to-atom arrival rate ratios, the ion energy must be large for noticeable densification, whereas at a high ion-to-atom arrival rate ratio, only a small ion energy is required.

If metal ions bombard the film instead of noble gas ions, the probability for ion incorporation is almost one because of equal mass momentum transfer and the attractive part of the

FIG. 11. MD simulation (2D) of a Ti film growing ($E_i = 50$ eV; $j_i/j_A = 0.16$): (a) with Ti atoms arriving only at thermal energy, (b) with Ti atoms arriving at thermal energy and 16% Ar^+ ions at 50 eV, and (c) with Ti atoms arriving at thermal energy and 16% Ti^+ ions at 50 eV.

FIG. 12. Density of a Ti film (calculated by MD simulation) as a function of the energy of coirradiating Ar^+ ions, for various ion-to-atom arriving rate ratios j_I/j_A .

metal-ion to -atom interaction. In Fig. 11(c) all the arriving Ti ions are implanted in the film.

Figure 13 displays the Ti film density as a function of the ion-to-atom arrival rate ratio j_I/j_A for an ion energy of 50 eV. The film attains maximum density for arrival rates $j_I/j_A > 0.2$, a ratio which we actually believe to have according to preliminary measurements.

IV. DISCUSSION

We can understand the film formation process of low-voltage reactive ion plating deposition and the resulting film

FIG. 13. Density of a Ti film (calculated by MD simulation) as a function of the ion-to-atom arrival rate ratio j_I/j_A of coirradiating Ti^+ ions of 50 eV.

FIG. 14. Extended structure zone model of thin-film structure as a function of the normalized substrate temperature T/T_m , to include the vitreous phase observed with reactive ion plating coatings (zone 4).

properties qualitatively by an extension of the classical structure zone model of Movchan and Demchishin⁶ with a zone 4 (Fig. 14), representing the vitreous phase of dielectric coatings found in this investigation. Thermal spiking on a local atomic level because of the conversion of kinetic energy of the electrostatically attracted ions into thermal energy gives rise to nominally very high temperatures (1 eV $\approx$ 11 000 K), which are quenched immediately by the cold environment (substrate and growing film, even when at 250 °C!) and the low thermal capacity of the species involved.

The randomly oriented microcrystallites found in the electron micrographs of ZrO_2 layers (Fig. 5) resemble the structure sketched in Fig. 14 for zone 3. The reason for this nonvitreous structure may be the higher melting point of ZrO_2 ($T_m = 2715$ °C) as compared with TiO_2 ($T_m = 1825$ °C) or Ta_2O_5 ($T_m = 1877$ °C), for which a vitreous phase was found in ion plated films also. If we assume a fictive substrate temperature T for ion plating of perhaps 2000 °C (Table II), bringing the normalized substrate temperature T/T_m for TiO_2 above, for ZrO_2 , however, below unity, the observed microstructures of these two film materials would accord to the model. Interesting test cases for this model would be thin films of Al_2O_3 and Y_2O_3 (which we

TABLE II. Melting points T_m of various oxides and the ratio T/T_m for substrates temperatures $T = 300$ °C (realistic for RE) and 2000 °C (fictive for RIPD).

Material	T_m [°C]	T/T_m [K/K] for	
		$T = 300$ °C	$T = 2000$ °C
SiO_2	1470	0.33	1.30
TiO_2	1825	0.27	1.08
Ta_2O_5	1877	0.27	1.06
Al_2O_3	2045	0.25	0.98
Y_2O_3	2226	0.23	0.91
ZrO_2	2715	0.19	0.76
HfO_2	2758	0.19	0.75

have not investigated yet as to their properties when deposited by reactive ion plating deposition) with T/T_m values close to unity (at the fictive substrate temperature of 2000 °C, representative of a certain set of process parameters for reactive ion plating deposition). With the T/T_m close to the boundary of Zone 4 for superthermal film formation ($T/T_m = 1$), one could predict obtaining either one of the structures (vitreous or polycrystalline) as a result of minor changes of process parameters determining the energy and/or arrival rate ratio of the ionized species.

SiO₂ (quartz) with a low melting point of $T_m = 1470^\circ\text{C}$ and inherent glass forming qualities was found to form amorphous films even with standard electron beam evaporation^{4,5,35} on heated substrates at about $T = 300^\circ\text{C}$. At this substrate temperature, electron beam evaporated SiO₂ would already exceed the boundary of the normalized substrate temperature $T/T_m \approx 0.3$, growing with a more dense but still columnar structure representative of zone 2. Although a distinct—even dense—columnar structure has never been observed to the best of our knowledge, electron beam evaporated SiO₂ may well grow in a densely packed structure of very thin columns (filaments) of diameters below the useful resolution of currently used electron microscopes and preparation techniques. This assumption is supported by the observation of elliptical water vapor penetration patterns in electron beam evaporated SiO₂ films deposited at an oblique angle of vapor incidence.³⁶ Similar experiments would be useful to carry out with reactive ion plating deposited thin films, as an independent method of establishing the micromorphology of these coatings.

The 2D molecular dynamics simulation of the growth of metal films (Ti) restricts certain degrees of freedom of the interacting particles. However, we believe that it reflects many of the essential features of a full 3D study. In 2D all the energy deposited into the film by an impinging ion is absorbed by a slab of only one atom thickness. Though the interaction strength between atoms is chosen to reproduce the cohesive energy in real bulk material, energy dissipation and displacement of atoms is overemphasized and, for example, a 25-eV ion will have a similar effect as a 100-eV ion on a realistic 3D film.

The MD simulation of film growth of metal-oxides is hindered by the complicated and ill-defined covalent interaction between species which would require an impractical amount of computer time for its calculation. The resulting film microstructure for a metal-oxide in a 3D simulation is expected for its simulation to be vitreous, when slow molecules together with fast ions arrive at a cold substrate. The glassy structure is quenched in by the incoming ions, which create high-temperature heat pulses which very rapidly expand and decay due to their cold surrounding. The extremely short quench time, the creation of disorder, and the presence of covalently bonded atoms of different sizes favor the appearance of such a vitreous state. In the above simple 2D MD simulation where particles interact via a spherically symmetric potential, a glassy structure is unstable and cannot appear. Recently, MD simulations of Si ion-beam deposition have indicated the formation of a vitreous state in a covalently bonded material.^{37,38}

V. CONCLUSIONS

We investigated the microstructure of several dielectric coatings, primarily TiO₂ single layers of various thickness, by means of transmission electron microscopy, Talystep surface profiling, and Raman microprobe. 2D molecular dynamics computer simulation of the elementary processes during the growth of a Ti thin film under coirradiation of either Ar⁺ or Ti⁺ ions of various energies and ion-to-atom arrival rate ratios aid in the understanding of the growth mechanisms leading to fully dense thin films. Based on the experimental results and this computer-aided modeling, we propose an extension of the classical structure zone model by Movchan and Demchishin with a zone 4, representing vitreous phases of TiO₂ and Ta₂O₅ thin films which we observed in the electron microscope investigation of their cross sections.

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