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A comparative study of the growth dynamics of zirconia thin films deposited by ionized jet deposition onto different substrates

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ABSTRACT

The use of ceramic coatings to improve mechanical, chemical, and biological properties of a large variety of materials including polymers and metals has often produced technologically attractive as well as problematic surfaces to study, because of their complicate morphology compared to smooth surfaces obtained, for example, by atomistic processes. In this work we deposited thin films of zirconia by a new generation pulsed electron deposition system named Ionized Jet Deposition onto four materials, different from each other by structure and surface texture, and applied methods of fractal geometry to investigate their microstructure and roughening mechanism at different thickness values. Our findings show that the film growth does not follow any known class of universality, but is strongly influenced by non-local effects inherent to deposition technique. In this context, we show that deposition onto rough materials is dominated by a strong memory effect that leads to uniform surface coverages that microscopically retain the shape of the substrate. This circumstance is potentially useful for deposition of conformal coatings in view of applications of such plasma-based deposition technique to cases of technological interest.

1. Introduction

Thin films with ceramic structure are currently used to improve magnetic, optical, electrical, mechanical or biological properties of the surface of a given material; solar cells, flat screens, cutting tools constitute some typical applications. In biomedical field, thin films based on zirconium oxide (zirconia, ZrO_2) are widely used because of their resistance to fracture [1,2] and intrinsic ability of promoting adhesion and proliferation of bone cells if compared to normal implantable devices used in orthopedics and dentistry [3,4]. There are some well-established techniques for depositing zirconia films such as sol-gel deposition [5], deposition of metallic organic vapors [6], pulsed laser deposition (PLD) and magnetron sputtering [7]. Recently, nanostructured thin films of zirconia reported to reduce the wear and plastic deformation of the ultra-high molecular weight component in a common junction system have been deposited by the pulsed electron deposition method [8, 9]. However, it is highly desirable that, in view of its application as a coating material with advanced mechanical properties, both the growth mode and the microstructure of deposited films must be under fine control. In each of the above-mentioned applications, optimization of the growth conditions to produce thin ceramic film with a controlled microstructure is thus extremely important. In particular, it is well established that substrate roughness can drastically affect the properties of a thin film. More precisely, roughness determines many functional properties of surfaces such as adhesion, friction [10] and wettability [11] since it encompasses morphological parameters such as size, spatial distribution, structure and composition of the surface features.

Nevertheless, technological applications often make use of non-conventional, typically “rough” substrates, as polymers [12–14] or metals [15–17]. In this field, ceramics have received poor attention and mainly qualitative characterization compared to surfaces produced by atomistic deposition processes, thus so far the growth of thin films onto unconventional substrates has not investigated in depth. Moreover, statistical parameters such as average roughness, root-mean-square (RMS) roughness and peak-to-valley ratio result not sufficient to a complete description of the surface because of their insensitivity to lateral structures, leading to identical conclusions for drastically different surface morphologies. Fractal analysis, thanks to its character of universality and intrinsically statistical nature, is able to connect vertical and lateral fluctuations within a wide spectrum of spatial frequencies [18], thus representing an ideal tool to investigate growth dynamics of rough surfaces without complications due to the expected high vertical fluctuations. In this paper, we used methods of fractal analysis to extract the micro-roughness parameters of thin ZrO_2 films deposited onto monocrystalline silicon, commercial glass slide and two

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materials largely used in the orthopedic field, e.g. a machined metal (Titanium grade 2) [19] and a polymer (PolyEtherEtherKetone or PEEK) [20]. The films were deposited at low rate and room temperature by a modified pulsed electron deposition method named Ionized Jet Deposition [21], and the growth evolution followed by Atomic Force Microscopy (AFM). Our findings significantly deviate from the well-established descriptions of film growth, as they do not fall into any known class of universality. In particular, we found that the growth is strongly affected by the angular distribution of the incident particle flux, which is at the origin of the observed rapid roughening via shadowing effect. Moreover, deposition onto rough surfaces is dominated by the roughness of the uncoated surface and the growth leads to formation of a homogeneous thin layer capable to retain the surface corrugation in the interval of thicknesses considered.

2. Materials and methods

2.1. Substrates

Deposition was carried out onto: 1) monocrystalline silicon with native oxide layer, p-type boron-doped, with resistivity 10 ÷ 15 Ω·cm, squared slides with size (10 × 10) mm^2 and thickness 0.6 mm (MicroFabSolutions s.r.l., Trento, Italy). RMS: (1.7 ± 0.4) nm at 50 × 50 μm^2 and (0.52 ± 0.16) nm at 3 × 3 μm^2 scale size. 2) Borosilicate glass microscope slides, squared with size (10 × 10) mm and thickness 1 mm (Fisher Scientific Gerhard Menzel, Braunschweig, Germany). RMS = (1.5 ± 0.3) nm at (50 × 50) μm^2 and (0.58 ± 0.18) nm at (3 × 3) μm^2 scale size. 3) Titanium grade 2, circular coupons with Ø = 10 mm and thickness 2 mm (courtesy of ISTEC-CNR, Faenza, Italy). RMS: (92 ± 13) nm at 50 × 50 μm^2 and (25 ± 9) nm at 3 × 3 μm^2 scale size. 4) Poly(etheretherketone) (PEEK) cubes having size ≈ 6 × 6 × 4 mm^3 (Direct Plastics Ltd., Sheffeld, UK). RMS: (125 ± 23) nm at 50 × 50 μm^2 and (18.6 ± 8.6) nm at 3 × 3 μm^2 scale size. All materials were used after ultrasonic cleaning in isopropyl alcohol for 5 min and then in milliQ water for additional 5 min.

2.2. Film deposition

Yttria-stabilized zirconia (ZrO_2) thin films were realized by the Ionized Jet Deposition system (Noivion Srl, Rovereto (TN), Italy) through the ablation of a tetragonal ZrO_2 target stabilized with 3 mol% Y_2O_3. Cylindrical targets (Ø = 30 mm, thickness = 7 mm) were fabricated starting from pure 3Y-TZP powder (Tosoh, Tokyo, Japan) by cold isostatic pressing (30 MPa, 1 min) and sintering at 1500 °C for 1 h (ISTEC-CNR, Faenza, Italy). The deposition was achieved through the ablation of the target mounted on a rotating target holder by a fast pulse (100 ns) of high energy (10 J) and high density (10^9 W·cm^{-2}) electrons. The ablated material was then directed toward the substrates mounted on a rotating holder and located at the distance of 10.0 cm from the target to obtain a homogeneous layer while a very low deposition rate (≈2–3 nm/min) is maintained. Due to the different thickness of the substrates, suitable supports were used for placing all them at the same distance from the target. The vacuum chamber was initially evacuated down to a base pressure of $1.0 \cdot 10^{-7}$ mbar by a turbo-molecular pump (EXT255H, Edwards, Crawley, England) and then raised by controlled flow of oxygen (purity level = 99.999%) to $1.2 \cdot 10^{-4}$ mbar. The working voltage and the electron beam frequency were set at 20 kV and 7 Hz, respectively. Depositions were carried out at room temperature, e.g. without heating the substrate holder. These deposition conditions were specifically optimized for the used target [22]. Depositions were carried out at 25, 50, 75, 100 and 150 min; the corresponding thickness values were measured onto silicon substrates (results not shown here) and reported where appropriate.

2.3. Atomic force microscopy measurements

The AFM images were acquired in air at room temperature and in tapping mode of operation using a stand-alone NT-MDT microscope (NT-MDT Co., Moscow, Russia), equipped with silicon cantilevers with typical tip curvature radius of 10 nm and resonant frequency around 240 kHz. All images were unfiltered, but leveled by a 2nd order line, and recorded at 512 × 512 pixels from several non-overlapped and random regions, with scan areas in the range of 1 to 50 μm^2. Due to samples large z-fluctuation, it was necessary to average RMS values from 7 to 15 images at each scan area to maintain the error bars smaller than 5–10%. All of the power spectra are based on the AFM images of 3 × 3 μm^2 scans. To avoid systematic errors due to surface anisotropy, spectra were acquired at different rotation angles of the sample, and then averaged. More specific details about data sampling and processing are provided further. We refer to films deposited onto silicon, glass, titanium and PEEK as Z-S, Z-G, Z-T and Z-P respectively.

3. Theory

On a self-affine surface, the RMS (or interface width) evolves with the image size L as a power law:

$$\sigma(L) \propto L^{\alpha}. \tag{1}$$

In most cases, the (1) exhibits an onset or “knee”, and the corresponding value $L = \xi^*$ is called system correlation length. α is called *Hurst* (or *static*) exponent, and is related to the surface texture. For $L \gg \xi^*$, the surface heights are no longer significantly correlated and the roughness is expected to saturate at the value σ_{sat}. For a time series of saturating curves σ(L), as for a set of surfaces obtained at different deposition times, the relation:

$$\sigma_{sat}(t) \propto t^{\beta} \tag{2}$$

holds, and β is called *growth* exponent. The relation 2) is expected to reach a saturation valuee to w_{sat} at a certain $t = t_{sat}$, hence from a time series of saturating σ(t) curves the β exponent can be estimated by the linear fit of the Log-Log plot of $\sigma_{sat}(t)$ at $t \ll t_{sat}$. The exponents α and β are related to each other by their ratio α/β = z which is called *dynamic* exponent.

Traditionally, high-resolution surface techniques such as AFM are used to estimate α, β and z by recording images at various scan size and plotting σ(L) and $\sigma_{sat}(t)$ on Log-Log scale; finally, the scaling theory assigns to α, β and *z* the class of universality of the growth process [23]. An equivalent approach to scaling uses Power Spectral Density (PSD) [24]. For a given image with N rows and M columns the 1D-PSD is evaluated by means of the Fast-Fourier Transform as:

$$P(K_x) = \frac{2\pi}{NMh} \sum_{j=0}^{N} |P_j(K_x)|^2, \tag{3}$$

where h is the sampling step, i.e. the distance between two adjacent image points and K_x is the component along the x-axis of the vector K in the reciprocal (or frequency) space. The j-th coefficient of the sum is given by:

$$P_j(K_x) = \frac{h}{2\pi} \sum_{k=0}^{N} z_{kj} exp\left(-iK_x kh\right), \tag{4}$$

where z_{kj} is the height of the image point having coordinates (k,j). With regard to the algorithm used for its calculation, $P(k_x)$ is provided for each line along the “fast” scan direction and the 512 curves so obtained are averaged together to obtain P(k) or pseudo 2D-PSD [25]. In our case this procedure has provided reproducible spectra able to effectively describe the statistic of the surface and to minimize the effects of tip convolution. The PSD curves exhibit typical features consisting of a plateau at low spatial frequencies with an onset at $k = \xi^{-1}$, and a monotonic decrease at higher frequencies. Pure 2D-PSD calculated onto