Natural and induced growth of VO₂\(^{(\text{M})}\) on VO₂\(^{(\text{B})}\) ultrathin films

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This work examines the synthesis of single phase VO₂\(^{(\text{B})}\) thin films on LaAlO₃(100) substrates, and the naturally-occurring and induced subsequent growth of VO₂\(^{(\text{M})}\) phase on VO₂\(^{(\text{B})}\) films. First, the thickness (t) dependence of structural, morphological and electrical properties of VO₂ films is investigated, evidencing that the growth of VO₂\(^{(\text{B})}\) phase is progressively replaced by that of VO₂\(^{(\text{M})}\) when t > ~11 nm. This change originates from the relaxation of the substrate-induced strain in the VO₂\(^{(\text{B})}\) films, as corroborated by the simultaneous increase of surface roughness and decrease of the c-axis lattice parameter towards that of bulk VO₂\(^{(\text{B})}\) for such films, yielding a complex mixed-phase structure composed of VO₂\(^{(\text{B})}\)/VO₂\(^{(\text{M})}\) phases, accompanied by the emergence of the VO₂\(^{(\text{M})}\) insulator-to-metal phase transition. Second, the possibility of inducing this phase conversion, through a proper surface modification of the VO₂\(^{(\text{B})}\) films via plasma treatment, is demonstrated. These natural and induced VO₂\(^{(\text{M})}\) phases not only provide substantial insights into the competing nature of phases in the complex VO₂ polymorph system, but can also be further exploited to synthesize VO₂\(^{(\text{M})}\)/VO₂\(^{(\text{B})}\) heterostructures at the micro/nanoscale for advanced electronics and energy applications.

Vanadium dioxide (VO₂) is a particularly interesting polymorphic material family that exists under several forms including VO₂\(^{(\text{A})}\), VO₂\(^{(\text{B})}\), VO₂\(^{(\text{M})}\), VO₂\(^{(\text{M1})}\) and VO₂\(^{(\text{M2})}\)\(^{(\text{M3})}\). Even though the chemical formula remains the same, VO₂ can assume various crystalline symmetries and electronic structures that exhibit different electronic and optical properties on account of strong correlation. This diversity of polymorphs makes VO₂ a promising electronic material and an excellent candidate for technological applications such as batteries, optical and electronic switching devices, IR sensors, smart windows and tunable metamaterials. VO₂\(^{(\text{M})}\) and VO₂\(^{(\text{B})}\) are the most desired VO₂ polymorphs as they display large changes in their electrical resistivity with temperature.

VO₂\(^{(\text{M})}\) is stable at room temperature and exhibits a monoclinic structure with the P2₁/c (14) space group and lattice parameters a = 5.75 Å, b = 4.54 Å, c = 3.98 Å and β = 122.6°. It undergoes a structural first-order reversible insulator-to-metal transition (IMT) at a critical temperature of T\(_{\text{IMT}}\) ≈ 68 °C to a VO₂\(^{(\text{R})}\) rutile structure with the P4\(^{(\text{2})}/\text{mmm}\) (136) space group and corresponding lattice parameters a = b = 4.55 Å and c = 2.85 Å. This transition is accompanied by sharp changes of both electrical resistivity and infrared reflectivity. The VO₂\(^{(\text{M})}\) phase is characterized by V-V dimerization, and alternatively short (~2.65 Å) and long (~3.12 Å) V-V bonds. The VO₂\(^{(\text{B})}\) metastable phase assumes a monoclinic layered structure similar to that of V₆O₁₃ with the C2\(/m\) (12) space group and lattice parameters a = 12.03 Å, b = 3.69 Å, c = 6.42 Å and β = 106.6°. Unlike VO₂\(^{(\text{M})}\), the decrease of the VO₂\(^{(\text{B})}\) electrical resistivity across the phase transition occurs gradually over a very broad range of temperatures, decaying by ~4 orders of magnitude when heating from ~123 °C to 127 °C. This transition is characterized by a change in the structure from a monoclinic semiconducting phase to another monoclinic semi-metallic phase. While the layered structure is maintained across the transition, the distance between neighboring V⁴⁺ ions slightly decreases, the reduction being larger for the ions in the (ac) plane, which represent half of the cations in the VO₂\(^{(\text{B})}\) structure.

Recent experiments have demonstrated the possibility to synthesize textured VO₂\(^{(\text{B})}\) thin films via pulsed laser deposition by lattice matching with SrTiO₃ (001) and LaAlO₃ (100) substrates. These results indicate that the thinnest VO₂\(^{(\text{B})}\) films do not contain any VO₂\(^{(\text{M})}\) phase and that the fraction of VO₂\(^{(\text{M})}\) phase increases with the film thickness. However, the mechanism that governs the emergence of the VO₂\(^{(\text{M})}\) phase and its distribution among the VO₂\(^{(\text{B})}\) phase remains unclear. Besides their individual properties, combining the properties of the two phases by co-growing these VO₂ polymorphs or by designing and fabricating VO₂\(^{(\text{M})}\)/VO₂\(^{(\text{B})}\) heterostructures has the potential to exploit the unique properties of the individual phases for enhanced functionalities.
(B) heterostructures could be exploited for future optoelectronic materials with tunable properties suitable in advanced electronic and energy devices.

Herein, we first investigate the structural, morphological and electrical properties of VO₂ thin films of various thickness (3 nm ≤ t ≤ 38 nm) grown on LaAlO₃ (100) (LAO) substrates. We demonstrate that the growth of distorted monoclinic VO₂ (B) metastable phase breaks at a critical thickness (tₐ) between 11 and 25 nm. Beyond that critical thickness, the strain-induced structural change further promotes the growth of the VO₂ (M) phase, which in turn results in the presence of a complex mixed-phase structure composed of VO₂ (B) and VO₂ (M) and in the appearance of the VO₂ (M) insulator-to-metal phase transition. We further exploit this behavior and demonstrate the possibility to tailor the growth of VO₂ polymorphs by modifying the properties of an ultrathin VO₂ (B) film via treatment of the film surface with an argon plasma. This process significantly modifies the vanadium valence state at the VO₂ (B) film surface and further promotes the growth of the VO₂ (M) phase.

Results
Natural growth of VO₂ (M) on VO₂ (B). The quality of the VO₂/LAO thin films was evaluated by acquiring XRD diffraction patterns of films with thicknesses ranging from 3 to 38 nm, as shown in Fig. 1(a). An interesting modification of the structure with thickness is observed. A detailed analysis reveals the presence of VO₂ (B) (00l) peaks for film thickness between 3 and 25 nm, which suggests that the films are highly oriented along this
direction. However, the thickest film (38 nm) behaves differently, with the intensity of the VO$_2$ (B) (00$l$) peaks being significantly smaller, while two other peaks appear at $2\theta$ = 27.8° and 42.2°. These angles correspond to the Bragg angle of the (011) and (210) orientations of the VO$_2$ (M) phase, respectively. All the other peaks coincide with reflection planes from the LAO substrate. The lower intensity observed for the VO$_2$ (M) (011) and (210) peaks in the diffractogram of the 38 nm-thick film as compared to those of the VO$_2$ (B) (00$l$) peaks in the diffractograms of the thinner films (3–25 nm) is due to the difference in both the diffracting planes Miller indices and crystalline structure between VO$_2$ (M) and VO$_2$ (B) phases. Accordingly, the structure factor ($F$) associated with each of these phases diffracting planes is different, and so is the diffracted intensity ($I \propto F^2$). For films with thickness below or equal to 25 nm, all peaks located at $2\theta$ = 14.4°, 28.9°, 44.0° and 60.0° (corresponding to the Bragg angle of VO$_2$ (B) (001), (002), (003) and (004) orientations respectively) show a full width at half maximum (FWHM) that decreases with increasing thickness, while their intensity increases and their position shifts to higher $2\theta$ values.

The presence of well-defined thickness-interference (Kiessig) fringes in the X-ray reflectivity (XRR) curves of Fig. 1(b) indicates that the film surface is smooth and the film-substrate interface well defined$^{20}$. The film thickness ($t$) can thus be calculated from these XRR curves from equation (1)$^{21}$.

**Figure 2.** Thickness dependent morphological properties of VO$_2$ films. AFM images of (a) 3, (b) 5, (c) 11, (d) 25 and (e) 38 nm-thick VO$_2$ thin films grown on LAO substrates. (f) RMS surface roughness as a function of film thickness. The white and black rectangles in (e) represent the rough and flat regions, which have a large RMS roughness and a RMS roughness comparable to that of the thinnest VO$_2$ films (a–c), respectively.
$$t = \frac{(m-n)\lambda}{2(\sin\theta_m - \sin\theta_n)}$$

Where $m$ and $n$ are the orders of interference, and $\theta_m$ and $\theta_n$ are the corresponding diffraction angles, respectively. The thickness values obtained from the XRR measurements are consistent with those determined from the cross-section SEM images of a VO$_2$ test sample. Figure 1(c) shows the c-axis parameter and the FWHM of the XRR curve.

**Figure 3.** Thickness dependent electrical properties of VO$_2$ films. Temperature-dependent resistivity of 5, 11, 25 and 38-nm thick VO$_2$ thin films grown on LAO substrates for heating (red curve) and cooling (black curve) segments using a van der Pauw geometry.

**Figure 4.** Effect of surface modification by plasma treatment on the morphological properties of the VO$_2$ films. AFM images of the (a) untreated (5 nm UT) and (b) plasma-treated (5 nm T) 5 nm-thick VO$_2$ thin films on LAO substrate and of the 5 nm-thick VO$_2$ films deposited on (c) untreated (10 nm UT) and (d) plasma-treated (10 nm T) 5 nm-thick VO$_2$ thin film surface.
of the (002) peak. The c-axis parameter gradually decays from 6.63 Å for the 3 nm-thick film to 6.44 Å for the 25 nm-thick film, which closely corresponds to the theoretical value of bulk VO\(_2\) (B) (\(c_B = 6.42\) Å), while its FWHM decreases from 2.14° to 0.39°. The decrease of the c-axis parameter means that the strain in the VO\(_2\) films is gradually released as thickness grows.

The observed thickness-dependent behavior of the VO\(_2\)/LAO system can also be illustrated by observing the film surface topography. The AFM images of Fig. 2(a–e) indicate that the thinnest films (3 to 11 nm) are very smooth. On the other hand, the thicker films (25 and 38 nm) show the presence of some regions with granular morphology along with other regions where the surface remains flat. Accordingly, as depicted in Fig. 2(f), the RMS surface roughness of the films increases with thickness with a more drastic change (from \(\approx 0.7\) to \(\approx 4.5\) nm) between 11 and 25 nm. The presence of distinctive regions characterized by different morphologies on the surface of the 25 and 38 nm-thick films is evidenced in Fig. 2(d–e). More specifically, for the 38 nm-thick film (Fig. 2(e)), the measured RMS roughness increases from 0.81 nm for the flat region (black rectangle), in agreement with the measured values for the thinnest VO\(_2\) (B) films, to 6.94 nm for the rough region (white rectangle). Combining both AFM and XRD analysis strongly suggests that these rough regions are composed of VO\(_2\) (M) phase nanocrystallites that grow at the expense of the VO\(_2\) (B) phase.

Figure 3 shows the electrical resistivity of the VO\(_2\) films with different thicknesses as a function of the temperature for both heating and cooling. The resistivity of the 3 nm-thick film could not be measured as it was beyond the upper detection limit of the system over the available range of temperatures. Such behavior most likely originates from an early stage VO\(_2\) film growth that is driven by Volmer-Weber island-type mechanism \(^{22,23}\), which is characterized by the formation of unconnected separated islands. The film discontinuity therefore prevents the

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**Figure 5.** Effect of surface modification by plasma treatment on the structural properties of the VO\(_2\) films. X-ray diffraction 0-20 patterns of the untreated (5 nm UT) and plasma-treated (5 nm T) 5 nm-thick VO\(_2\) thin films on LAO substrate and of the 5 nm-thick VO\(_2\) films deposited on the untreated (10 nm UT) and plasma-treated (10 nm T) 5 nm-thick VO\(_2\) thin film surface.

**Figure 6.** Effect of surface modification by plasma treatment on the vanadium valence state content of the VO\(_2\) films. (a) XPS spectra of the V2p\(_{3/2}\) peak deconvoluted into V\(^{5+}\), V\(^{4+}\), V\(^{3+}\) and V\(^{2+}\) peaks and (b) vanadium valence content of the untreated (5 nm UT) and plasma-treated (5 nm T) 5 nm-thick VO\(_2\) thin films on LAO substrate and of the 5 nm-thick VO\(_2\) films deposited on the untreated (10 nm UT) and plasma-treated (10 nm T) 5 nm-thick VO\(_2\) thin film surface.
formation of a current pathway between the electrical contacts and rules out the possibility to reliably measure the 3 nm-thick VO₂ film resistivity. The monotonous resistivity decrease with increasing temperature for the thinnest films (5 and 11 nm) is accompanied by a small hysteresis at low temperature, in agreement with the typical behavior of VO₂ (B) thin films. On the other hand, for the 38 nm-thick VO₂ film, the temperature-dependent resistivity behaves like that of VO₂ (M) phase as it decreases from 9.14 Ω cm at T = 20 °C in the insulating state to 0.96 mΩ cm at T = 105 °C in the metallic state. This provides evidence of the presence of the typical VO₂ (M) insulator-to-metal transition with transition temperatures T_{IMT(h)} = 70.6 °C for the heating cycle and T_{IMT(l)} = 63.8 °C for the cooling cycle, as calculated from the d(log(σ))/dT curves. The average transition temperature is therefore T_{IMT} = 67.2 °C, a value similar to that of bulk VO₂ (M) (T_{IMT} ≈ 68 °C), while the hysteresis width is 6.8 °C. Finally, the 25 nm-thick film exhibits a monotonous decrease of the resistivity in the temperature range [-90 °C – 55 °C], in agreement with the VO₂ (B) phase behavior. However, at T ≈ 65 °C, this film shows an abrupt decrease of its resistivity (from 40 mΩ cm to 6 mΩ cm), as observed for the VO₂ (M) phase.

Overall, the thickness dependence of the phase of the VO₂ thin films deposited on LAO substrates clearly indicates that the exclusive growth of VO₂ (B) ceases at some critical thickness where the growth of highly-oriented metastable monoclinic VO₂ (B) films is no longer possible. Beyond that thickness, the monoclinic VO₂ (M) phase appears and the films are then composed of a mixture of VO₂ (B) and VO₂ (M) polymorphs.

The VO₂ (B) monoclinic structure observed for the thinnest VO₂ thin films results from the good lattice matching and from the corresponding consistent strain with the LAO substrate. For films thicker than 11 nm, removing this strain through the creation of dislocations and defects strongly modifies locally and randomly the film surface morphology. Accordingly, the growth of the VO₂ (B) polymorph is prevented, which promotes that of the VO₂ (M) polymorph and leads to the coexistence of both VO₂ (B) and VO₂ (M) phases for films with thickness t > t_c. These observations therefore indicate that strain significantly influence the competing nature of VO₂ polymorphs growth, so as it does for the ultrafast structural transition dynamics following above-gap photoexcitation. Likewise, they strongly suggest that the surface properties of the VO₂ (B) film, which play a key role in the observed phase growth change from VO₂ (B) to VO₂ (M), should definitely be considered to further control the growth of these polymorphs. Indeed, a local modification of the surface of the VO₂ (B) films, which is very smooth for the thinnest VO₂ films, could locally be induced to promote the growth of the VO₂ (M) phase in specific regions.

**Induced growth of VO₂ (M) on VO₂ (B) ultrathin films.** To explore the possibility of inducing the growth of the VO₂ (M) phase, a 5 nm-thick VO₂/LAO sample displaying only the VO₂ (B) phase was exposed to an argon plasma to modify its surface. In this experiment, performed at 20 °C, half of the sample surface was covered by a bare LAO substrate and the full sample was further exposed for 30 seconds to an argon plasma at a pressure of 10 mTorr with a substrate bias of 135 V. This experiment, which enables to expose only half of the ultrathin VO₂ film as the other half remains as deposited, also ensures that the properties of the VO₂ film surface are absolutely identical prior to the plasma treatment. After plasma treatment, the bare LAO substrate was removed and another 5 nm of VO₂ was deposited over the whole sample. This yields on one half of the sample a 10 nm-thick untreated VO₂ film and on the other half a mixed 10 nm-thick VO₂ film composed of a 5 nm-thick treated layer covered with a 5 nm-thick untreated layer.

The morphological (AFM) and structural (XRD) properties of each half of the VO₂ film were characterized prior to and after plasma treatment, and also after the second VO₂ deposition. Figures 4 and 5 show the surface morphology and diffraction patterns of the untreated film (5 nm UT), of the treated film (5 nm T), of the film deposited on the untreated surface (10 nm UT) and of the film deposited on the plasma-treated surface (10 nm T). It is observed that plasma treatment modifies neither the VO₂ film growth nor the RMS roughness of the surface. Indeed, the topography of both 5 nm UT (Fig. 4(a)) and 5 nm T (Fig. 4(b)) is flat and smooth with small RMS roughness values of 0.32 nm and 0.29 nm, respectively. The structural properties are also unaffected by the plasma treatment as the diffractograms of both 5 nm UT and 5 nm T films exclusively display VO₂ (B) (00 l) peaks. Nevertheless, a slight intensity reduction is observed for the VO₂ (B) (00 l) peaks present in the diffractogram of the 5 nm T film with regards to that of the 5 nm UT film. This small intensity reduction could result from a plasma treatment-induced surface amorphization within the top first few atomic layers of the 5 nm T film. While the surface morphology of the 10 nm UT film (Fig. 4(c)) remains similar to that of the 5 nm UT and the 5 nm T films with only a slightly higher RMS roughness of 0.42 nm, that of the 10 nm T film (Fig. 4(d)) is significantly modified. In this case, the surface is covered with nanograins and its RMS roughness increases to 9.86 nm. In addition, the structural properties of the 10 nm T film are significantly altered as compared to those of the 10 nm UT film. Indeed, as shown in Fig. 5, the intensity of the VO₂ (B) (00 l) peaks of the 10 nm T film significantly decreases as compared with that of the three other films while the VO₂ (M) (011) peak emerges. Clearly, these effects exclusively result from the plasma treatment of the underlying VO₂ ultrathin film, which indicates that this treatment has induced a modification of the growth mechanisms. Interestingly, these effects are also similar to those previously observed when the thickness of the VO₂ films is increased from 11 nm to 38 nm so as to exceed the critical thickness.

**Origin of the induced growth.** To further gain insight in the mechanisms governing the phase growth change induced by plasma treatment, X-ray photoelectron spectroscopy (XPS) was performed on the four samples (5 nm UT, 5 nm T, 10 nm UT and 10 nm T). The V2p3/2 core level binding energy was used to characterize the oxidation state of vanadium. Therefore, the vanadium valence state content of the VO₂ films was determined at each step of the process by deconvoluting the V2p3/2 peak in a combination of V^{2+}, V^{4+}, V^{3+} and V^{5+} Gaussian/Lorentzian peaks, as depicted in Fig. 6(a). The position of these peaks was ascribed to 517.4 eV, 516.1 eV, 514.1 eV and 512.9 eV, respectively and the spectra were fitted using the CasaXPS software and a Shirley function to
remove the background. The vanadium valence state content of the VO₂ films shown in Fig. 6(b) was calculated from the ratio of the integrated areas of the V⁴⁺, V⁵⁺, V⁶⁺ and V⁷⁺ peaks.

The spectrum of the 5 nm UT film is mainly due to the V⁵⁺ (39.4%) and V⁴⁺ (57.7%) valence states with negligible contribution from V³⁺ (2.9%) and none from V²⁺ valence states. It is similar to that of the 10 nm UT film, but strongly differs from that of the 5 nm T film. Indeed, the latter film shows a broader XPS spectrum that is shifted to lower binding energies, so that the contribution from the V⁵⁺ valence state is strongly reduced to 11.1% and that of the V⁴⁺ valence state is enhanced from 2.9% to 32.4%, while a small contribution from the V²⁺ valence state (2.5%) appears. For the 10 nm T film, the spectrum width shrinks back and returns to higher binding energies, like 5 nm UT and 10 nm UT films. Accordingly, the main contributions come from the V⁵⁺ (54.6%) and V⁴⁺ (43.1%) valence states while the V³⁺ valence state negligibly contributes (2.5%) and the V²⁺ not at all. One can therefore conclude that plasma treatment strongly modifies the surface chemical states of the ultrathin VO₂ (B) film, lowering the contribution of the higher valence state (V⁵⁺) and enhancing that of the lower valence states (V⁴⁺ and V³⁺). This indicates a larger amount of oxygen vacancies at the surface, which favors the growth of the VO₂ (M) phase as compared to that of VO₂ (B). Furthermore, even though the stoichiometry and chemical states of the VO₂ (B) film are significantly modified by plasma treatment, the stoichiometry of the subsequently grown VO₂ film is preserved.

The change of phase growth induced by plasma treatment strongly affects the structural and morphological properties of the VO₂ ultrathin film. Indeed, the 2D growth of pseudomorphic metastable VO₂ (B) film exhibiting a flat surface topography switches to a 3D island-type growth of stable VO₂ (M) nanocrystallites with rough surface, forming a VO₂ (B)/VO₂ (M) composite structure. These effects are very similar to those observed when the VO₂ film thickness is increased beyond the critical thickness lying between 11 and 25 nm. However, tailoring the phase growth offers the possibility to spatially control both the size and location of the emerging VO₂ (M) phase regions using for example a patterning method such as lithography. In contrast, natural phase growth results in randomly distributed phase mixtures. Tailoring the phase growth could thus be exploited to control the VO₂ structure at the nanometer scale through the onset of spatially controlled VO₂ (M) islands in a VO₂ (B) ultrathin film, paving the way to the synthesis of various VO₂ (M)/VO₂ (B) complex heterostructures.

Conclusions

In conclusion, by investigating the morphological, structural and electrical properties of VO₂ films grown on LAO substrates with various thickness (3 nm ≤ t ≤ 38 nm), the growth of single pseudomorphic distorted metastable monoclinic VO₂ (B) phase was shown to change once a critical thickness lying between 11 and 25 nm is reached. This strain-induced change of structural phase growth is accompanied by the increase of surface roughness and by the appearance of the stable VO₂ (M) phase. The thicker films exhibit a complex mixed-phase structure composed of VO₂ (B) and VO₂ (M) polymorphs and undergo the typical VO₂ (M) first-order phase transition at T_{IMT} ≈ 68 °C. By modifying the VO₂ (B) ultrathin film using plasma treatment, the possibility to induce this change of phase growth was demonstrated and further related to a strong modification of the vanadium valence state on the VO₂ (B) film surface and to the corresponding creation of oxygen vacancies. Natural or induced phase growth change not only provides a stimulating environment for investigating the fundamental issues related to the complex competing nature of the VO₂ polymorphs, but also presents a strong potential for the fabrication of VO₂ (M)/VO₂ (B) heterostructures at the nanoscale. This opens new opportunities of applications in the field of advanced electronics and energy where nanostructured electronic materials with tunable properties are required, as well as for the design of metamaterials for optoelectronic applications.

Methods

Sample growth. Reactive pulsed laser deposition (RPLD) was used to fabricate VO₂ thin films by ablating a commercial vanadium metal target (99.95% purity, KJ Lesker). The films were deposited on LaAlO₃ (100) substrates. The growth temperature was 550 °C and the oxygen pressure was kept at 21 mTorr. The detailed growth conditions were reported in a previous study.

XRD, AFM, XPS and electrical characterization. The structural properties of the films were examined by X-ray diffraction (XRD) in the 0–2θ configuration, between 10° and 65°, and in the X-ray reflectivity (XRR) configuration using a PANalytical’s X’Pert PRO Materials Research Diffractometer with Cu Kα radiation operated at 45 kV and 40 mA. The film thickness was determined by cross-section scanning electron microscopy (SEM, JEOL JSM-7401F) on a test sample and by X-ray reflectivity. The surface morphology of the films was imaged by atomic force microscopy (AFM, DI-EnviroScope, Veeco) while X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG Escalab 2201-XL system with Al Kα (hv = 1486.6 eV) radiation. The resistivity of the films was measured in van der Pauw geometry using a Quantum Design physical properties measurement system (PPMS) and a cryostat. The electrical contacts (100 nm Au/300 nm Cu/5 nm Cr) were deposited at the corners of the samples using e-beam evaporation.

Surface treatment by argon ions. Surface treatment was achieved in a cylindrical Inductively Coupled Plasma reactor (ICP) from Oxford instruments (Plasmalab 100, model ICP 380). In this system, the ICP plasma was generated at a frequency of 2 MHz and the power was set at 1 kW. The kinetic energy of the ions was controlled by applying 13.56 MHz RF power on the chuck table, yielding a bias voltage of 135 V. The experiments were carried out in pure Ar and the gas pressure (10 mTorr) was controlled by means of a throttling valve located at the bottom of the processing chamber.

Data availability. The data that support the findings of this study are available from the corresponding author on request.
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Author Contributions

N.É. prepared the VO\(_2\) samples and performed the XRD, XPS and electrical measurements. B.T. performed the AFM measurements. N.É. analysed the data. N.É. and B.T performed the surface treatment of the film. The manuscript was prepared by N.É. with assistance from B.T. and M.C. All the authors discussed the results. M.C. directed the overall project.

Additional Information

Competing Interests: The authors declare no competing interests.

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