Optimisation study of the synthesis of vanadium oxide nano-structures using pulsed laser deposition

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ABSTRACT

Fast imaging plasma plume study have been carried out on vanadium-oxygen plasma generated using 248 nm, 25 ns pulses from an excimer KrF laser under oxygen atmosphere. The plume expansion dynamics of an ablated VO_2 target was investigated using a fast-imaging technique. The free expansion, splitting, sharpening and stopping of the plume were observed during these oxygen pressures, 0.01, 0.05, 0.10 and 0.20 mbar. The influence of the plume dynamics study on the properties of the obtained vanadium oxide thin films were examined using X-Ray Diffraction method. A vanadium dioxide phases were deposited at 0.05 mbar oxygen pressure for target-substrate distance of 40 mm and 50 mm. Mixed phases of vanadium oxide were deposited at 0.01, 0.10 and 0.20 mbar oxygen pressure for target-substrate distance of 40 mm. Transition temperatures of around 60.9°C have been measured from sample deposited at 0.05 mbar oxygen pressure for target-substrate distance of 50 mm. We observe mixed nanostructures for thin film prepared at 0.05 mbar for target-substrate distance of 40 mm, while the thin film prepared at 0.05 mbar for target-substrate of 50 mm shows an uniform nanostructure film.

Keywords: Plasma plume, Vanadium dioxide, XRD, Optical switch.

1. INTRODUCTION

Vanadium dioxide (VO_2) is electrically conducting at a temperature higher than 68°C and is insulating at a temperature lower than 68°C [1]. Due to this behaviour, VO_2 has been presented as an attractive material for electrical or optical storage, laser protection and solar energy control for windows in space satellites [2]. VO_2 nanoparticles and thin films are preferable to bulk VO_2 due to the fact that they can survive the stress generated during repeated cycles of phase transition and their transition temperature can be modified to near room

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temperature by doping [3, 4]. Several studies have been done in order to deposit such material as thin films [4]. However, it is difficult to synthesise a monoclinic VO_2 nanostructure with a well-defined size and morphology using pulsed laser deposition method because there are several stable vanadium oxide phases; a synthesis protocol is needed to ensure the formation of pure VO_2 phase [5, 6]. Therefore it is important to understand the laser plasma interaction and plasma plume expansion during a pulsed laser deposition process of synthesising the VO_2 nanostructures thin films.

In pulsed laser deposition (PLD) process, it is important to control the plume dynamics in order to obtain good quality and correct stoichiometry thin films or nanostructures. Basically, in order to able to control the laser-induced plasma plume, a good understanding of the basic physics and chemistry associated with laser-target and particle-particle interaction within the laser-induced plasma plume is needed. Pulsed, laser intensity is used to heat and vaporize the material of interest in vacuum [4]. In this process, the plasma formed by the leading edge of the laser pulse will be heated efficiently by the rest of the laser pulse. For the case of the nanosecond, long pulse laser ablation, the plasma expands isothermally during the laser pulse followed by adiabatic expansion after the laser pulse termination [7, 8]. During the isothermal regime process, initially the laser interacts with the target and low temperature plasma plume is formed, collisional ionization and excitation, coupled with the remainder of the laser pulse energy rapidly heats and ionizes the plasma. However the plasma expands freely into vacuum during adiabatic expansion regime process.

Various groups using a variety of plasma diagnostic tools have extensively studied the entire process of nanosecond laser ablation, plasma formation and expansion, and also have extensively modelled the processes [9]. An atmospheric gas is always used as a moderator for energetic particles in pulsed laser deposition process [10]. The presence of the atmospheric gas influences the entire processes of plasma generation as well as expansion. The plume expansion in the presence of a background gas leads to the internal plume structures, plume splitting, sharpening, confinement, instead of free expansion in vacuum. Several studies have shown that the plasma plume expansion process depended on laser intensity, pulse duration, wavelength of the laser, target material and geometry, and the nature and pressure of any background gas [11]. The plasma characteristics also vary with distance from the target surface as well as with time following the onset of plume formation. Lafane et al. [12] studied the correlation of plume dynamics and oxygen pressure with VO_2 stoichiometry during PLD by ablating vanadium pentoxide (V_2O_5) target. They highlighted the effect of the plume dynamics on the properties of the obtained vanadium oxide thin films and found that the splitting into two components and a slowdown of the plume appear, coinciding with the appearance of the pure VO_2 phase in the deposited films at this pressure 4 x 10^{-3} mbar. Therefore, the plasma plume dynamics under background gas remains an interesting field to study in order to understand the complex physico-chemical mechanisms.

In this study, we study the mechanism of the plasma formation and expansion during the PLD process of vanadium oxide, since the source of the films is a laser generated plasma composed of neutral and ionised atoms, molecules and other species. The plume expansion dynamics of an ablated target of VO_2 was investigated using a fast-imaging technique. Fast imaging technique is one of the versatile diagnostic tools for understanding the expansion dynamics of laser created plume especially when the plume interacts with an ambient gas [9]. The light may be imaged onto an intensified charge coupled device (ICCD) by a lens for the study of plume dynamics as the ablated material is transported from the target to deposition substrate. This time-resolved and spatially-resolved information is very useful as the deposited film properties and quality can depend on the kinetic energies of the plume constituents. And also the light may be coupled via a lens/fibre to a spectrograph with an ICCD camera. In this way one can obtain information on the plume constituents such as atoms, ions, molecules, clusters and particles and their state. Thin films were deposited using the same gas pressure condition as for the plasma dynamics study in order to investigate the relationship between the plume dynamics study and the properties of the obtained vanadium oxide thin films using X-Ray Diffraction (XRD).

2. EXPERIMENTAL DETAILS

The experimental setup was used to carry out the study of the plume expansion dynamics of ablation plume of VO_2 in this study has already described in previous work [13, 14]. During the experiments, the vacuum chamber was initially evacuated to a base pressure of 10^{-5} mbar and thereafter oxygen was introduced. The substrate was positioned and faces parallel to the target. The overall emission of the bright expanding plasma was recorded by means of fast ICCD camera, from the start of the target-laser ablation event, up to the arriving of the ablated species onto the substrate. Two cylindrical lenses are used to focus the KrF (λ = 248 nm, τ = 25 ns) laser beam on the rotating target with an incident angle of 45^o. The target was a VO_2 pellet. A set of spherical, plane mirrors and a Zeiss lens (76 mm focal length, spectral range: 350 – 800 nm) were used to image the two-dimensional luminous plasma on the ICCD camera (Princeton Instruments PI-MAX, 1024 x 256 pixel size = 26 x 26 μm) with a magnification of 1/3. The temporal resolution of the ICCD camera is 5 ns and its spectral response is within the range of 190 – 850 nm. The plasma plume study was carried out at vacuum pressure and at a range of oxygen gas pressures (0.20, 0.10, 0.05, 0.01, 0.004 and 0.001 mbar). The pulsed energy was fixed at 120 mJ which gives a laser fluence of 2 Jcm^{-2}. The number of accumulation, ICCD gain and gate were adjusted for each image to compensate for the reduction of the plume intensity during the expansion.

Thin films were deposited on glass at a pulse repetition rate of 5 Hz for 10 minutes under the same pressure and pulse energy conditions as that used for the plasma plume study. The target-substrate distance was set to 40 mm. The substrate temperature was set to 600 ^{o}C.

3. RESULTS AND DISCUSSION

3.1 Plume dynamics

In order to better understand the influence of oxygen pressure on the structural and morphological properties of the deposited VO_2 thin films, we have studied the V-O plasma plume dynamics generated by laser ablation. 2D images of visible V-O plasma plume emission measured at different delays following the laser pulse into vacuum and several oxygen pressures taken by ICCD camera are given in figure 1 (a) and figure 1 (b). All the 2D images were measured for all visible emission within 350 – 800 nm of the plume excited species, with the spectral range being limited by the objective lens. At vacuum and low pressures $<10^{-2}$ mbar, the plasma plume expands freely without any external viscous force. The effect of background gas on the expansion dynamics begins at 10^{-2} mbar< pressures and resulting in the plume splitting and enhancement of intensity.

For oxygen pressure <0.004 mbar the plume expand freely from early to the late time delay. This means that there is no plume to oxygen gas boundary appears as shown in figure 1 (a). However, in this oxygen pressure ranges 0.01 mbar to 0.20 mbar, the plume is confined and splits into two components at time delays that depend on the oxygen pressure as shown in figure 1 (b). Several authors [14, 15] have observed the plume splitting and have different opinions [16]. Wood et al. [17] discussed this phenomenon based on the combination of multiple elastic scattering and hydrodynamics formulations. The splitting of the plasma plume into two components indicates the interaction between the plume species which are scattered in a backward direction after collisions with background gas molecules and the incoming particles [18]. The results of this interaction are the formation of a shock front and enhancing of the plume luminosity at the plume to oxygen edge. Highly reactive atomic oxygen is produced in the shocked layer and oxygen enrichment in the deposited films is expected [19]. A shock wave may develop if the mass of the ablated material is lower than the mass of the surrounding

background gas the plasma plume had set in motion, and if the pressure driving the moving front of the plasma plume is greater than the pressure of the background gas at rest [20]. The development of the shock wave is indicated by the appearance of a visible edge at the contact front between the plasma and the surrounding gas. As time delays increases for 0.20 mbar to 0.05 mbar of oxygen pressure, we observed a sharpening of the plume as shown in figure 1 (b). Several authors reported on this sharpening of the plasma and they suggested that the plume sharpening mean that high kinetic energy particles are emitted closed to the target surface normal [21]. The plume sharpening was attributed to the slowing down of a part of the plasma plume due to the interaction with background gas.

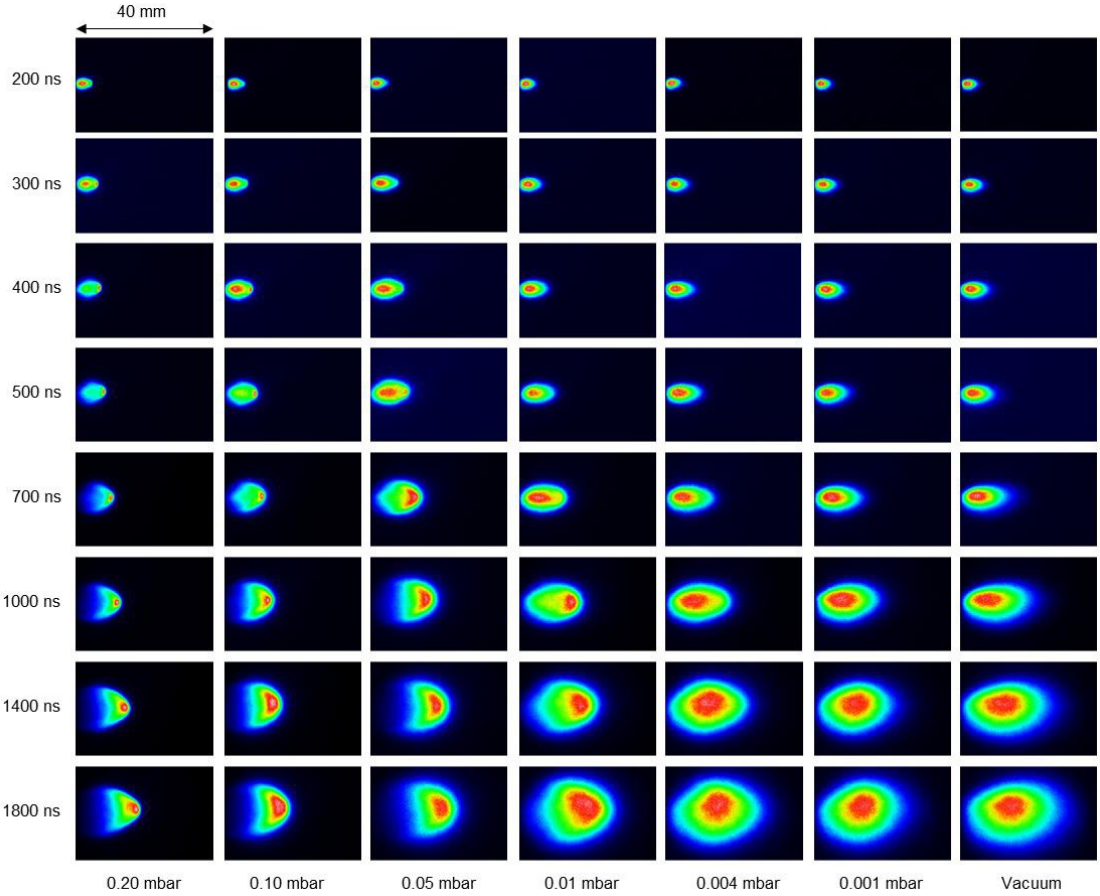

Figure 1 (a): The temporal of the visible plume for several oxygen pressure taken during laser ablation of the VO_2 target.

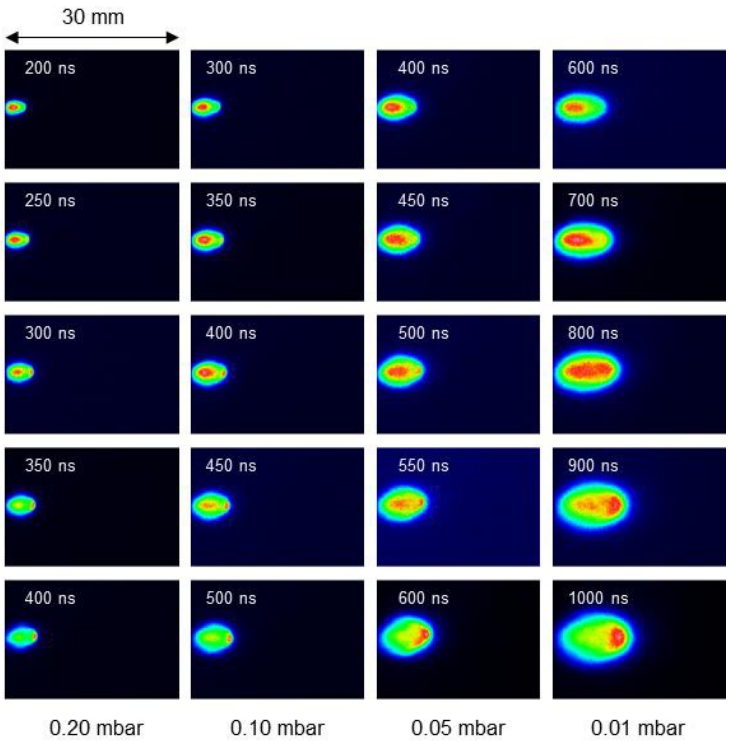

Figure 1 (b): The temporal of the visible plume for several oxygen pressure taken during laser ablation of the VO_2 target.

In order to study the plasma plume expansion dynamics, we plotted the plasma front position against time delays for the different oxygen pressure as shown in figure 2. We observed that the plasma plume expansion have the same behaviour at early time delays, which means that the plasma plume for various oxygen pressure propagate at the same speed. At these oxygen pressures 0.1, 0.2, 0.05, and 0.01 mbar, the expansion remains linear in the early time and the deviation increases with increasing time from free-plume emission expansion to plume emission slowing down. In this regime of the propagation, the ejected species collide with the oxygen gas molecules and lose their kinetic energy and later the plume emission stops completely. The ejected species diffuse into the oxygen gas until they reach a distance where they lose their kinetic energy. For 0.2 mbar oxygen pressure, the plasma plume expansion dynamics passes from free-like to shock-like and finally reaches a stopping time and distance. The other pressures it's out of the observation zone. We observe very low interaction at these oxygen pressures, 0.001 mbar and 0.004 mbar. The point of transition from one expansion regime to the next varies depending on the ambient gas pressure.

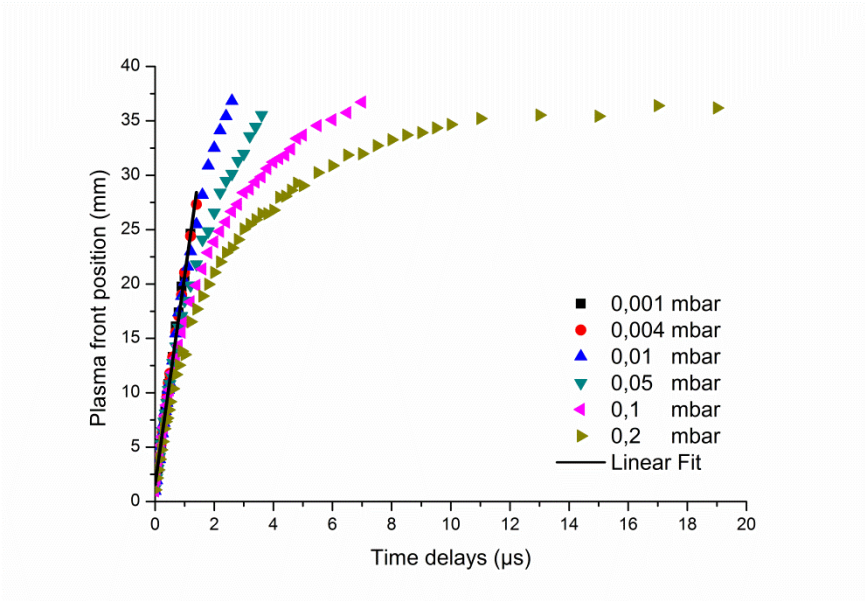

Figure 2: The plasma front position against time delays for the different oxygen pressure and vacuum.

3.2 Structural and switching properties

In order to verify the possibility to synthesise vanadium oxides compound by using a target VO_2, thin films were deposited at the same conditions of pressure and fluence used for the plasma study. A corning glass was used as a substrate in this study. The target-substrate distance was set at 40 mm for 0.05 mbar oxygen pressure for 10 minutes deposition time. The target-substrate distance was changed from 40 mm to 50 mm for 0.05 mbar oxygen pressure for 15 minutes deposition time and the rest of the oxygen pressure the target-substrate distance was set at 40 mm for 10 minutes deposition time. The substrate temperature was maintained at 600^{o}C and deposition time was 10 minutes. Figure 3 shows the XRD patterns of the films deposited under several oxygen pressures for target-substrate distance 40 mm. The deposited thin films show a significant difference in their crystalline structure. We observed a similar XRD patterns at high oxygen pressure which are mixed phases of VO_2, V_2O_3 and V_2O_5. These could be due to the influence of plasma plume dynamics: at high oxygen pressure there is high interaction between oxygen and plasma plume species. At 0.20 mbar oxygen pressure some XRD patterns intensity are low, while at 0.10 mbar the XRD patterns intensity are high. We observed some XRD peaks shift from19 to 20 degrees for 0.10 mbar and 0.20 mbar, respectively. We observed a similar weak XRD peak of V_2O_3 for both low oxygen pressures. At 0.01 mbar, we have pure phases of V_2O_3 and at 0.05 mbar; we have a strong VO_2 phase. This is understandable since, we mentioned early that at low pressure there is a little interaction of oxygen and plasma plume species. Figure 4 shows the XRD patterns of the films deposited at 0.05 mbar oxygen pressure for target-substrate distance of 40 mm and 50 mm, respectively. The XRD patterns show how the distance of target-substrate influences the vanadium oxide phases. As mentioned earlier, at 40 mm we observed a strong VO_2 phase and as the target-substrate distance changed to 50 mm, we observed another phase of VO_2 and two as yet unidentified peaks.

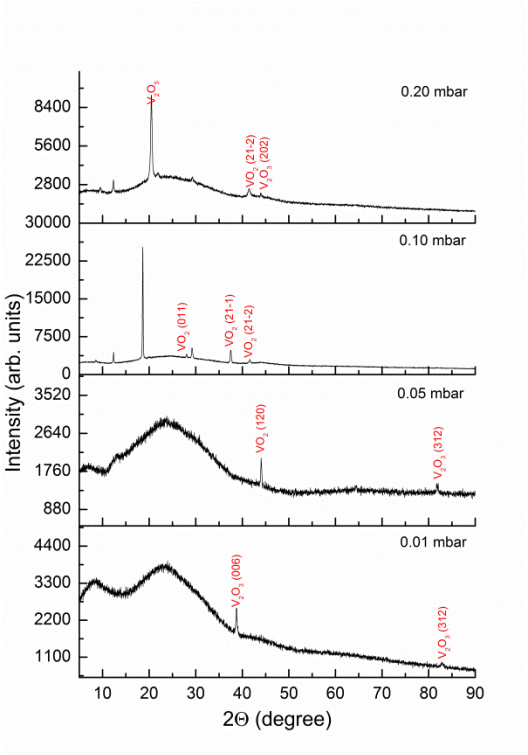

Figure 3: XRD patterns of the thin films deposited under several oxygen pressure for target-substrate distance of 40 mm.

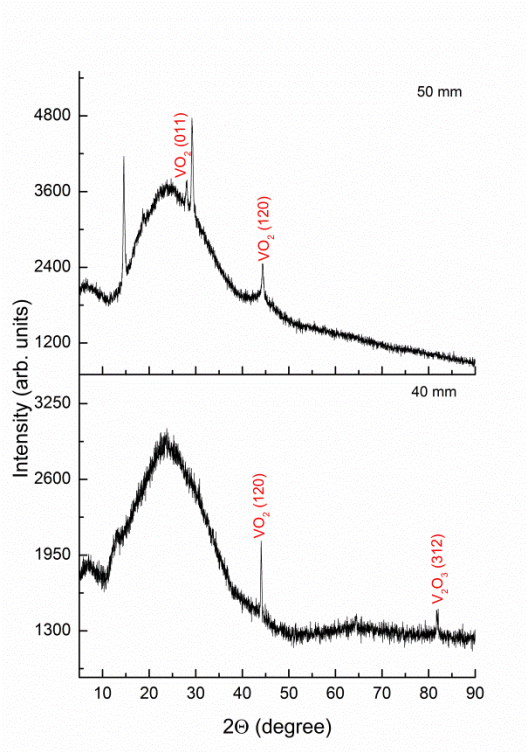

Figure 4: XRD patterns of the thin films deposited at 0.05 mbar oxygen pressure for target-substrate distance of 40 mm and 50 mm, respectively.

UV-Vis-IR transmittance spectroscopy is useful in revealing the switching properties of VO_2 from the room temperature monoclinic structure to a tetragonal rutile-type structure at above 68°C [1]. Figure 5 and figure 6 shows the thin films optical transmission as a function of wavelength of thin films deposited at 0.05 mbar for 40 mm and 50 mm target-substrate distance, respectively. The graphs show a rather small and large amount of switching for thin film deposited at 0.05 mbar for 40 mm and 50 mm, respectively. The differences in the transmittance of both thin films at different temperatures might due to the different phases of the vanadium oxides identified by XRD. Very poor switching was observed in sample deposited at 0.05 mbar oxygen pressure at 40 mm target-substrate distance as shown in figure 7. A completed different transition is observed in the thin film deposited at 0.05 mbar oxygen pressure for 50 mm target-substrate distance. A transition temperature of around 60.9°C for heating and 46.9°C for cooling were determined using figure 8. The role of target-substrate distance in the change of properties is shown. This result look promising since 60.9°C for heating up is close to 68°C. Our first goal is to optimise the transition temperature of VO_2 and to understand the influence of the plume expansion to the VO_2 structure and the influence of the VO_2 structure to the VO_2 transition temperature. Morphology studies were carried out using scanning electron microscope (SEM). Figure 9 and figure 10 are SEM morphologies of thin films prepared at 0.05 mbar for target-substrate distance of 40 mm to 50 mm, respectively. The morphologies show a mixed nanostructures for thin film prepared at 0.05 mbar for target-substrate of 40 mm, while the thin film prepared at 0.05 mbar for target-substrate of 50 mm shows an uniform nanostructure film. These seems to be in agreement with the transmittance of a thin film under temperature due to that for the thin film prepared at 0.05 mbar for target-substrate of 40 mm, we observed poor switching while the thin film prepared at 0.05 mbar for target-substrate of 50 mm, we observed good switching.

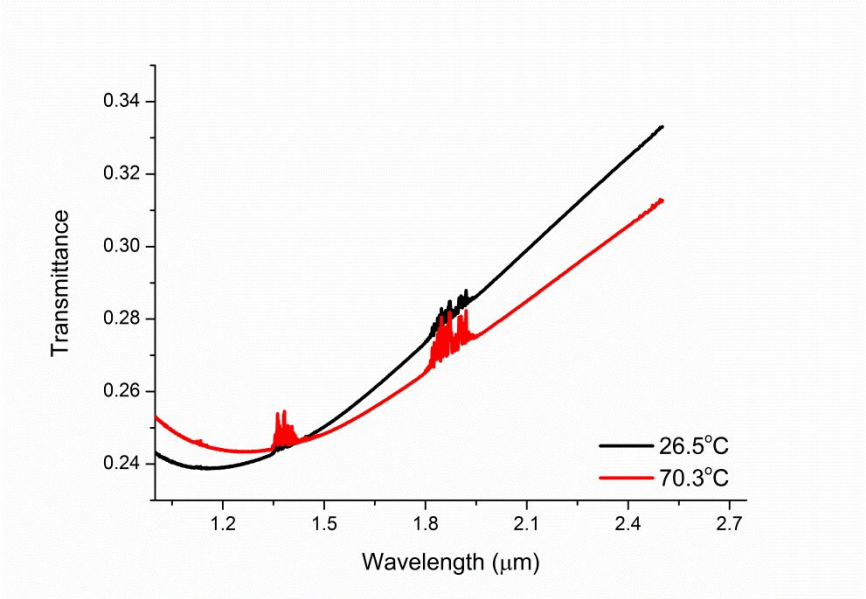

Figure 5: Transmittance at different wavelengths for thin film prepared at 0.05 mbar oxygen pressure for target-substrate distance of 40 mm.

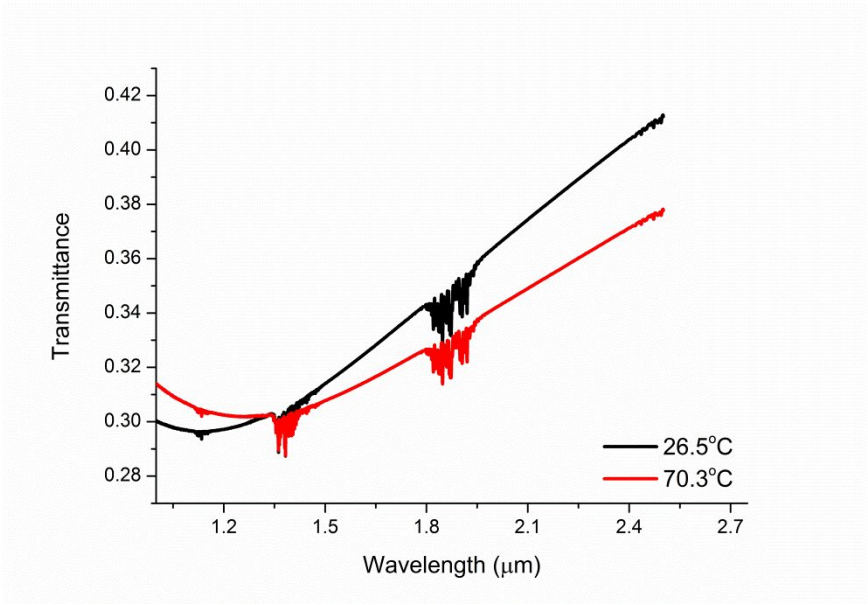

Figure 6: Transmittance at different wavelengths for thin film prepared at 0.05 mbar oxygen pressure for target-substrate distance of 50 mm.

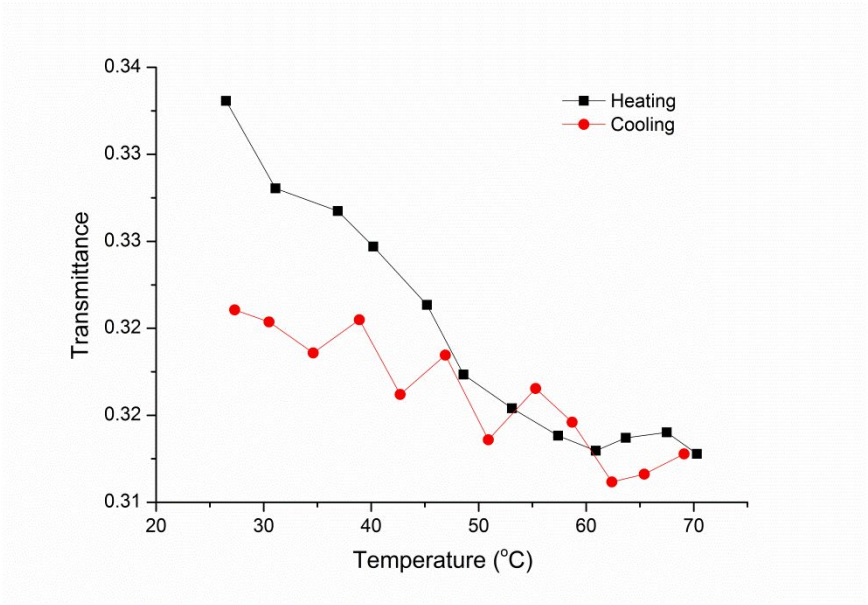

Figure 7: Change of transmittance at 2.5 μm due to semiconductor-to-metallic phase transition in VO_2 film deposited on corning glass substrate for target-substrate of 40 mm at 0.05 mbar oxygen pressure.

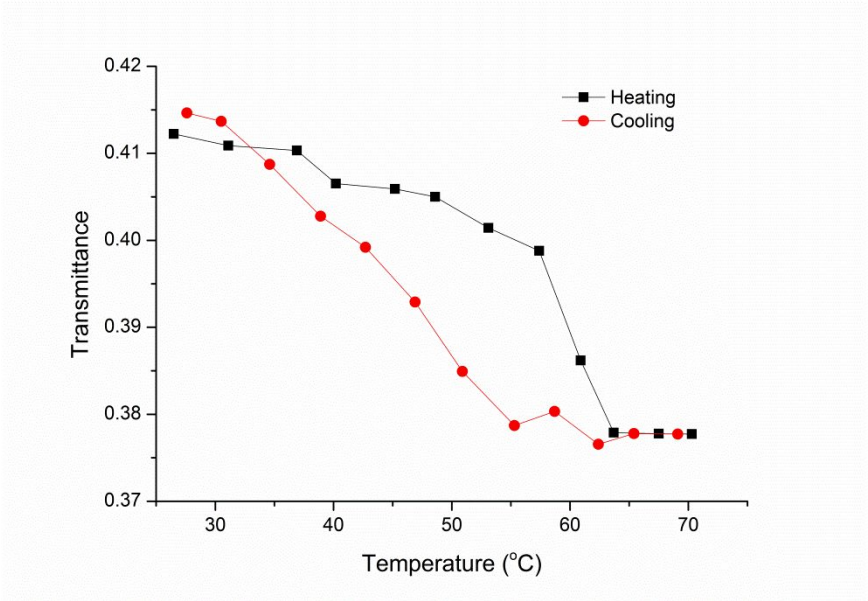

Figure 8: Change of transmittance at 2.5 μm due to semiconductor-to-metallic phase transition in VO_2 film deposited on corning glass substrate for target-substrate of 50 mm at 0.05 mbar oxygen pressure.

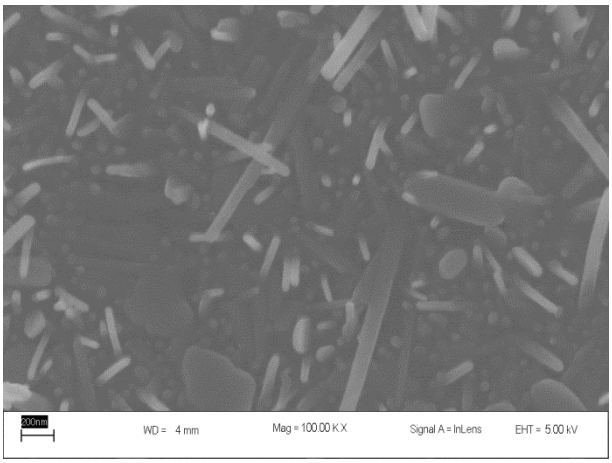

Figure 9: SEM morphology of a thin film prepared at 0.05 mbar oxygen pressure for target-substrate distance of 40 mm.

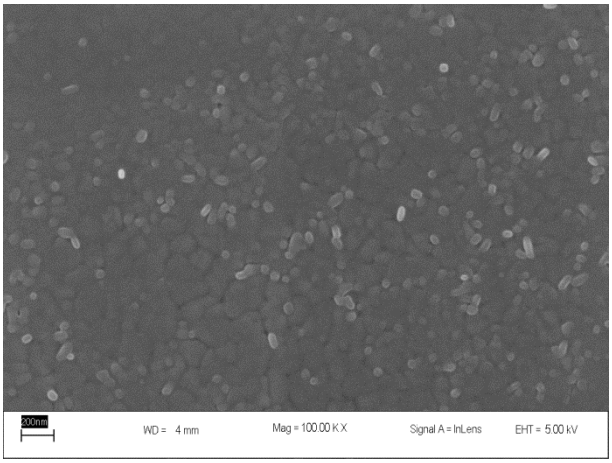

Figure 10: SEM morphology for a thin film prepared at 0.05 mbar oxygen pressure for target-substrate distance of 50 mm.

4. CONCLUSIONS

The expansion dynamics of an ablated target VO_2 oxide by KrF laser in background oxygen atmosphere has been investigated using an ICCD imaging. The ICCD images revealed several effects as plume splitting, sharpening and stopping. The time delay where each effect appears depends on the oxygen pressure. The deposited thin films under the same conditions of oxygen pressure and laser properties used for the plasma study, exhibit a pure V_2O_3 phase at oxygen pressure of 0.01 mbar, and others thin films are mixture of vanadium oxide phases. Transition temperatures of around 60.9^{o}C for heating and 46.9^{o}C for cooling have been measured from sample deposited at 0.05 mbar oxygen pressure for target-substrate distance of 50 mm. This is a first step to understand the influence of the plume expansion to the VO_2 structure and the influence of the VO_2 structure to the VO_2 transition temperature.

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