# *In-Situ* AlN Induced Valence State Variation of V in Vanadium Oxide Films Investigated by XPS

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**Abstract:** Vanadium oxide ($VO_x$) thin films with and without in situ AlN layer were grown on single crystal sapphire substrates by pulsed laser deposition (PLD) with $V_2O_5$ target. The significant structure and morphology transforms resulted from the insertion of *in-situ* AlN layer were observed by X-ray diffraction (XRD) and field-emission scanning electron microscope (FESEM). To interpret the mechanism behind these phenomena, the valence state variation of vanadium (V) in $VO_x$ films induced by *in-situ* AlN layer was investigated by X-ray photoelectron spectroscopy (XPS) analyses. The results indicated that the valence state of V become more complicated and $VO_x$ films with the mixed V valence state of $V^{5+}$,$V^{4+}$and $V^{3+}$ were obtained due to the introduction of AlN interfacial stress layer. Our achievements will be helpful for understanding the physical mechanism behind the exotic characteristics of $VO_x$ films induced by stress layer.

**Keywords:** Vanadium oxide ($VO_x$) thin films, pulsed laser deposition, valence state, X-ray photoelectron spectroscopy, AlN stress layer.

## 1. INTRODUCTION

It is well known that vanadium oxides ($V_2O_3$, $V_2O_5$, $VO_2$ and $V_6O_{13}$, etc.) undergoes a first phase transition at a critical temperature (Tc), accompanied by an abrupt change in its resistivity and near-infrared transmission [1]. Most notably, vanadium dioxide ($VO_2$) is especially interesting as it undergoes a reversible semiconductor-to-metal transition (SMT) phase transition at a critical temperature of 341 K (more close to room temperature), i.e., transformation from a monoclinic ($P2_1/c$) semi conducting state at low temperature to a tetragonal (rutile-$P4_2/mnm$) metallic state at high temperature [2,3]. Due to these distinct properties, $VO_2$ material shows high potential for various applications, such as electronic switches, thermal sensors, optical data storage disks, and thermochromic smart windows [4]. However, the SMT critical temperature of 341 K was still rather higher for its practical applications. So far, several methods were adopted to adjust its critical temperature (Tc) for various applications, such as doping with high-valent cations (such as $Nb^{5+}$, $Mo^{6+}$, $W^{6+}$) [5,6], engineering film stress [7-9] and changing crystalline size [10]. Nevertheless, few successful reports with satisfied performances were achieved due to the difficulty in controlling the valence state of V in vanadium oxide films and the ambiguity of SMT mechanism. Because of its half filled d-shell, V in vanadium oxide films possesses a set of valence states and prone to form a number of oxides (such as VO, $V_2O_3$, $VO_2$, and $V_2O_5$) with remarkable discrepancy in phase transition behavior [11]. Moreover, investigation of valence state variation of V in vanadium oxide films is also of great interest in condensed-matter physics because it is a classic strongly correlated electron system. It is well established that X-ray photoelectron spectroscopy (XPS) analyses is a powerful tool to investigate the valence state and local atoms arrangement in material, thus more insight into the physical mechanism behind the properties can be expected.

Up to now, various techniques have been employed to grow $VO_2$ thin films, such as pulse laser deposition (PLD), sol-gel process, metal organic chemical vapor deposition (MOCVD), and magnetron sputtering [2]. Among them, the PLD method is a well-established growth method for metal oxide thin films and nanostructures with high structural quality and well controlled chemical stoichiometry [12]. Since the atoms or clusters fabricated by the pulsed laser ablation are very energetic, it generally facilitates stoichiometry transfer of the chemical composition of a multi-element

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source target into the grown samples. Therefore, the PLD technique has been currently extensively investigated as a suitable way for $VO_2$ film epitaxial growth. However, the existence of a number of competing oxide phases with different V valence states offers a particular challenge to the application of vanadium oxides. There has been less report on the investigation of valence state variation of V in $VO_x$ films induced by *in-situ* AlN stress layer.

In this work, $VO_x$ thin films with and without in situ AlN layer were grown on single crystal sapphire substrates by PLD with $V_2O_5$ target. The significant structure and morphology transforms resulted from the insertion of *in-situ* AlN layer were observed. Particular attention has been dedicated to the valence state variation of V in $VO_x$ films induced by *in-situ* AlN layer, which was investigated by XPS analyses. An understanding of valence state variation of V in $VO_x$ films induced by stress layer will benefit the realization of high performance $VO_2$ based materials applications.

## 2. MATERIALS AND METHODS

VOx films were generally grown on single crystalline substrates with suitable lattice constants, such as sapphire or $TiO_2$ single crystalline substrates. In our current work, the $VO_x$ thin films with and without *in-situ* AlN stress layer (~ 20nm) were grown on c-sapphire substrates using PLD in an ambient of partially filled oxygen and argon. 2-inch circular vanadium pentoxide ($V_2O_5$) and AlN targets were ablated for the deposition. To investigate the effect of *in-situ* AlN stress layer, both samples were deposited under the same processing parameters. A pulsed laser beam generated by a KrF excimer laser (248 nm emission, Lambda Physik USA, Inc.) was introduced into the deposition chamber through a quartz window, and focused using an optical lens onto the target surface for laser ablation. The laser was operated at a repetition rate of 10 Hz and per pulse energy was 250 mJ. The targets were rotated at a speed of 15 rpm during the laser ablation process to avoid crater formation and ensure uniform ablation. The distance between the target and the substrate was 5 cm. The deposition chamber was initially evacuated using a turbo molecular pump to achieve a background pressure of the order of $10^{-6}$Torr. It was then backfilled with $O_2$ to obtain a suitable pressure for the deposition of each film. The substrate temperature during deposition of both AlN and $VO_2$ was kept at 600 °C. Prior to deposition, a 20mm×20mm sapphire substrate substrates were cleaned with a normal process to remove residual contaminants on its surfaces. Then the substrate was heated up to 600 $^oC$ to collect the laser plume to grow the $VO_x$ thin films with and without *in-situ* AlN stress layer. The samples with desired film thickness (~100 nm) were achieved by controlling the deposition duration according to our experience. After deposition, the substrates were slowly cooled to room temperature under the same deposition atmosphere as that used for growth. By this way, the residual thermal strain due to the difference in the thermal expansion coefficients of the film and substrate can be minimized.

The film samples were evaluated in terms of structure, morphology, and composition properties. The crystallographic properties of the thin films were determined by X-ray diffraction (XRD) using a D/Max-2400 ($CuK_{a1}$: $\lambda = 0.154056$ nm), the diffraction photons were collected by the diffractometer from 20 to $60^o$ with a $0.02^o$ step size. The surface morphology of the films was analyzed by a field-emission scanning electron microscope (FE-SEM) on JEOL JSM 6700F. The films composition and *in-situ* AlN induced valence state

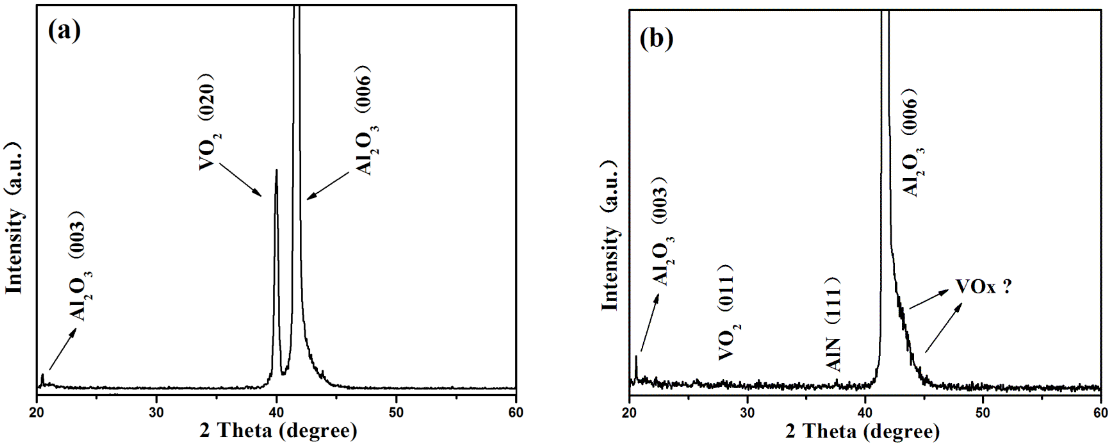

**Figure 1:** XRD patterns of samples with and without *in-situ* AlN layer grown on sapphire substrates by PLD at 1.5 pa $O_2$ partial pressure. (**a**) $VO_2$ films without *in-situ* AlN layer; (**b**) samples with *in-situ* AlN layer.

variation of V in VOx films were investigated by X-ray photoelectron spectroscopy (XPS) analyses on Thermo Scientific ESCALAB250Xi system with an $Al_{K\alpha}$ 1486.8eV X-ray radiation source under a base pressure of $3\times10^{-8}$ Pa, and a hemispherical energy analyzer was equipped on the system for energy detection. Before measurement, the sample was sputtered by Ar ion bombardment for 30 second for surface cleaning. The $C_{1s}$ binding energy line at 284.6ev was taken as a reference for calibration and the composition was calculated from the peaks areas taking into account the sensitivity factors. Fitting of the $V_{2p}$–$O_{1s}$ spectra was essential for determination of oxidation states of V present in the oxide layer. This was done after subtraction of Shirley background using Gaussian–Lorentzian sum function by XPSPEAK 4.1 software.

## 3. RESULTS AND DISCUSSION

### 3.1. The Crystallographic Structure of Samples with and without *In-Situ* AlN Stress Layer

Figure **1** shows the XRD patterns of $VO_x$ film samples with and without *in-situ* AlN layer grown on sapphire substrates by PLD at 1.5 pa $O_2$ partial pressure. Because of its half filled d-shell, vanadium element possesses a set of valence states and prefers to form a number of oxides such as VO, $V_2O_3$, $VO_2$, and $V_2O_5$. It has been demonstrated that the valence states of V in $VO_x$ films are very sensitive to the $O_2$ partial pressure during the PLD growth process, and thus high quality pure phase $VO_2$ films could be achieved only under a narrow window of the optimized $O_2$ partial pressure [4]. Here, $VO_x$ films with and without *in-situ* AlN layer were grown on sapphire substrates by PLD at 1.5 pa $O_2$ partial pressure according to our previous results [11]. As can be seen from Figure **1a**, in addition to the dominant diffraction peak at 41.67° which is corresponding to the sapphire (006) substrate, the very well-defined XRD pattern corresponding to the monoclinic $VO_2$ (020) was observed at 39.9°. No additional peaks due to other vanadium oxide phases are observed from the patterns, indicating that the high quality pure monoclinic phase $VO_2$ films with (020) preferred orientation was obtained on sapphire substrates without *in-situ* AlN layer. However, the crystalline quality degraded seriously as a result of the introduction of AlN interfacial stress layer. As demonstrated in Figure **1b**, in addition to the dominant diffraction peak corresponding to the sapphire

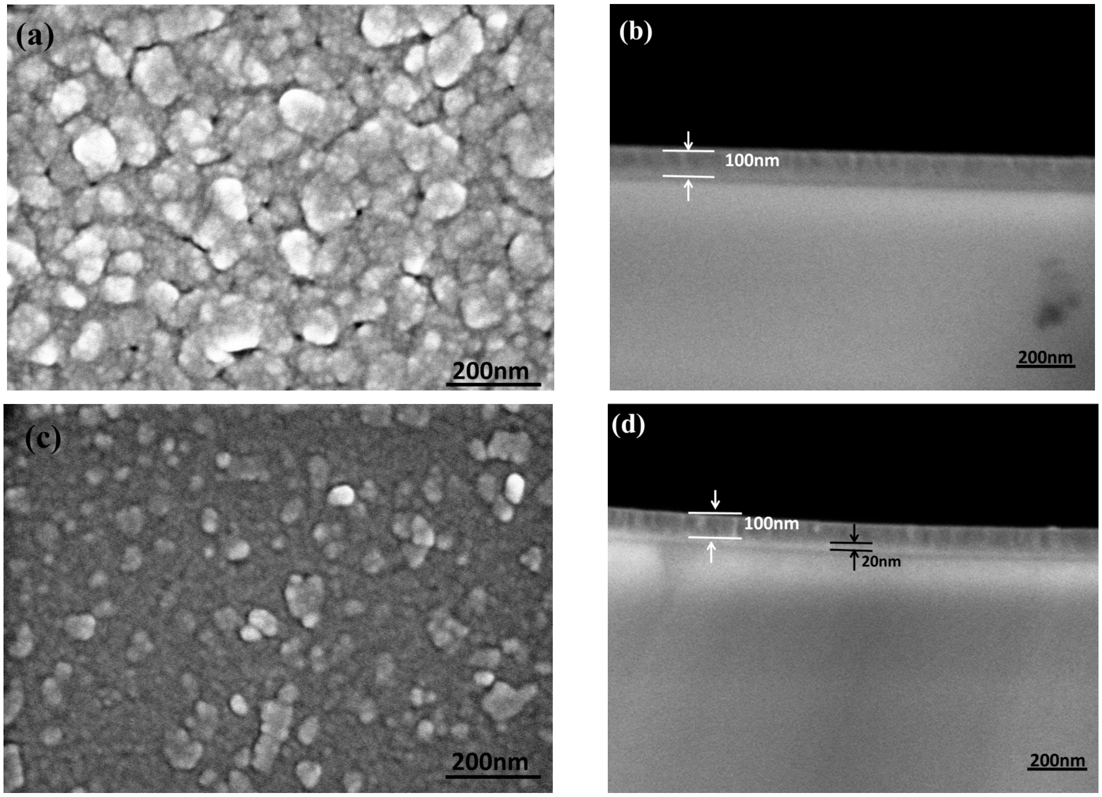

**Figure 2:** SEM images of samples with and without *in-situ* AlN layer grown on sapphire substrates by PLD: Surface (**a**) and corresponding cross-section (**b**) images for $VO_2$ films without *in-situ* AlN layer; Surface (**c**) and corresponding cross-section (**d**) images for samples with *in-situ* AlN layer.

substrate, the diffraction patterns consist of several rather weak diffraction peaks. Introducing the AlN stress layer leads to the broadness and ill-defined features of these XRD peaks, assignment of any individual peak to a specific $VO_x$ phase is difficult. Such a profile indicates a mixed amorphous-like or polycrystalline structures with very fine grains for the vanadium oxide film, as well as possible mixed phases of a number of competing vanadium oxide phases with different vanadium oxidation states such as $V_3O_5$, $V_2O_3$ or $V_2O_5$.Therfore, the drastically degraded crystalline quality of $VO_2$ films was assumed to be associated with the internal tensile strain along the in-plane axis caused by the lattice mismatch between AlN and $VO_2$.

### 3.2. The Surface Morphologies of Samples with and without *In-Situ* AlN Stress Layer

Figure **2** shows the SEM images of samples with and without *in-situ* AlN layer grown on sapphire substrates by PLD. As can be seen from Figure **2a** and **b**, the pure $VO_2$ films without *in-situ* AlN layer were composed of granular crystallites uniformly distributed on the sapphire substrate. The smooth surface with relatively uniform and dense grains distribution was obtained for the sample without *in-situ* AlN layer. A clear interface between sapphire substrate and $VO_2$ film can be observed from the cross-section image shown in Figure **2b**. In addition, the rather dense and compact structure with uniform thickness of 100 nm was also obviously observed. However, as AlN stress layer was introduced between $VO_x$ films and sapphire substrate, as shown in Figure **2c** and **d**, a much rougher surface was observed and some irregular grains were observed on the sample surface. A clear interface between sapphire substrate and AlN stress layer, as well as the interface between AlN stress layer and $VO_x$ film can be observed from the cross-section image shown in Figure **2d**. Moreover, the compact $VO_x$/AlN/Sapphire structure with uniform $VO_x$ film thickness of 100 nm and AlN layer of 20 nm were also demonstrated. The grain size for $VO_2$ film without in situ AlN layer is about 80 nm, which was much larger than its counterpart with in situ AlN layer (60 nm). These results indicated that the crystalline quality degraded drastically due to the insertion of AlN stress layer, which is in consistent with the XRD results in Figure **1** where the XRD peak varies significantly with the insertion of *in-situ* AlN layer.

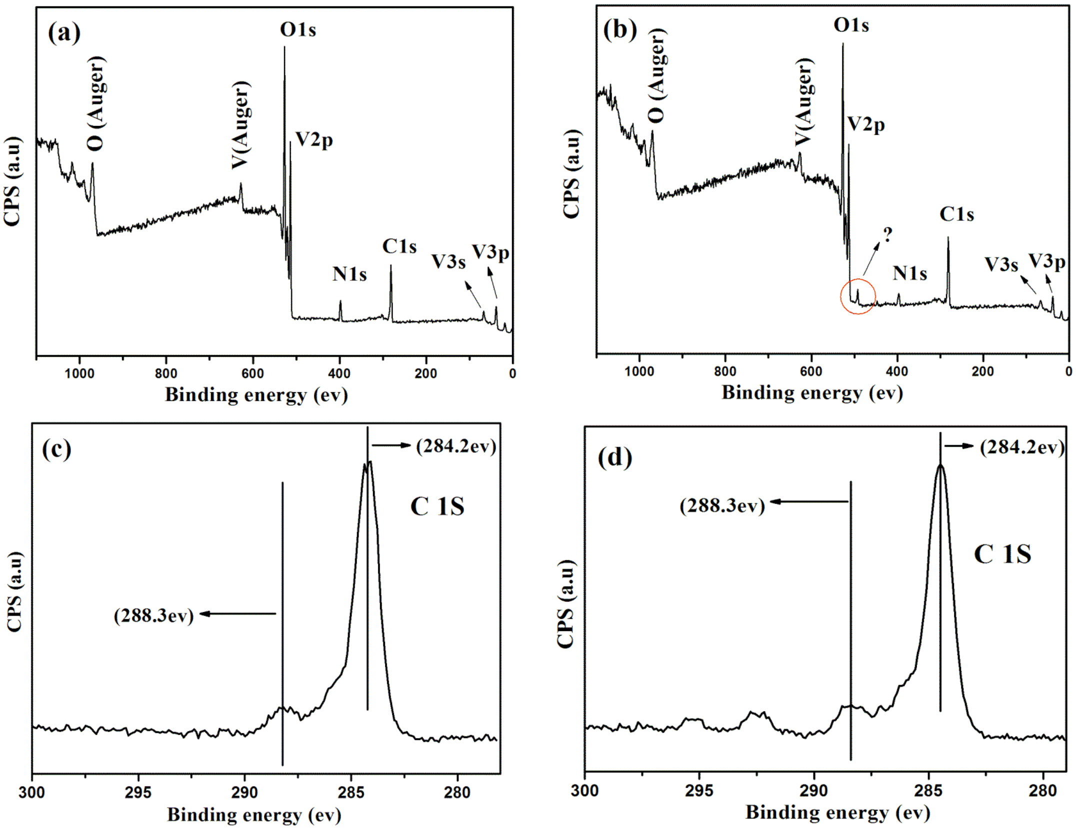

**Figure 3:** The XPS survey spectra of samples without *in-situ* AlN layer (**a**) and with *in-situ* AlN layer (**b**) grown on sapphire substrates by PLD, (**c** and **d**) are enlarged high-resolution spectra of C1s for binding energy calibration.

### 3.3. The Valence State Variation of V in VOx Films Investigated by XPS Measurements

XPS analysis was performed to detect the detailed components of as-grown films. Figure **3a** and **b** show the wide range XPS survey spectra between binding energy 0−1100 eV for samples with and without *in-situ* AlN layer grown on sapphire substrates by PLD. The signals from elements of vanadium (V), oxygen (O), carbon (C), and nitrogen (N) were detected for both samples with and without *in-situ* AlN layer grown on sapphire substrates by PLD. Figure **3c** and **d** are enlarged high-resolution spectra of C1s between 280 and 300 eV for binding energy calibration. The binding energy of C1s at 284.6 eV for both films can be attributed to hydrocarbons. The other peak located at higher binding energies (around 288.3) was attributed to the C-O bonds. After calibrated by C1s binding energy, the peaks in Figure **3a** and **b** were identified as follows according to previous reports in literature [2]: the peak at 516eV was attributed to $V^{4+}$ $2p_{3/2}$, the peak at 529.8eV is referenced to O1s line, Auger peaks from O and V were detected at 981 eV and 633 eV, respectively. The peaks at 69.3ev and 40 eV were attributed to V3s and V3p peak. No signals from underneath AlN layer were detected at any significant level from Figure **3b**, suggesting the penetration depth of X-ray was not enough for penetrate the $VO_x$ film. The detection of C and N can be ascribed to unintentionally contamination from environment during the growth and measurement process since C and N were ubiquitous element. No remarkable discrepancy was observed from the XPS survey spectra except that a weak unknown peak was detected at around 500 eV from Figure **3b**. The slightly higher V3s peak at 69.3 eV in Figure **3a** than the one in Figure **3b** was observed, indicating that the most oxidation state of V in the films is +4 (i.e. $VO_2$) rather than +5 (i.e. $V_2O_5$). As the V3s peak location for the pure $V_2O_5$ should be near 70 eV while for $VO_2$ the binding energy is 0.75 eV lower than that of $V_2O_5$[2,10].

Figure **4a** and **b** are the enlarged high-resolution spectra of O and V elements with the binding energy between 510 and 535 eV. Two distinct peaks located at around 516 eV and 523 eV were attributed to $V2p_{3/2}$ and $V2p_{1/2}$, respectively. To indentify the different valence states of V in $VO_x$ film induced by *in-situ* AlN stress layer, the well established Silversmit's method was adopted [13]. The O1s core level centered at

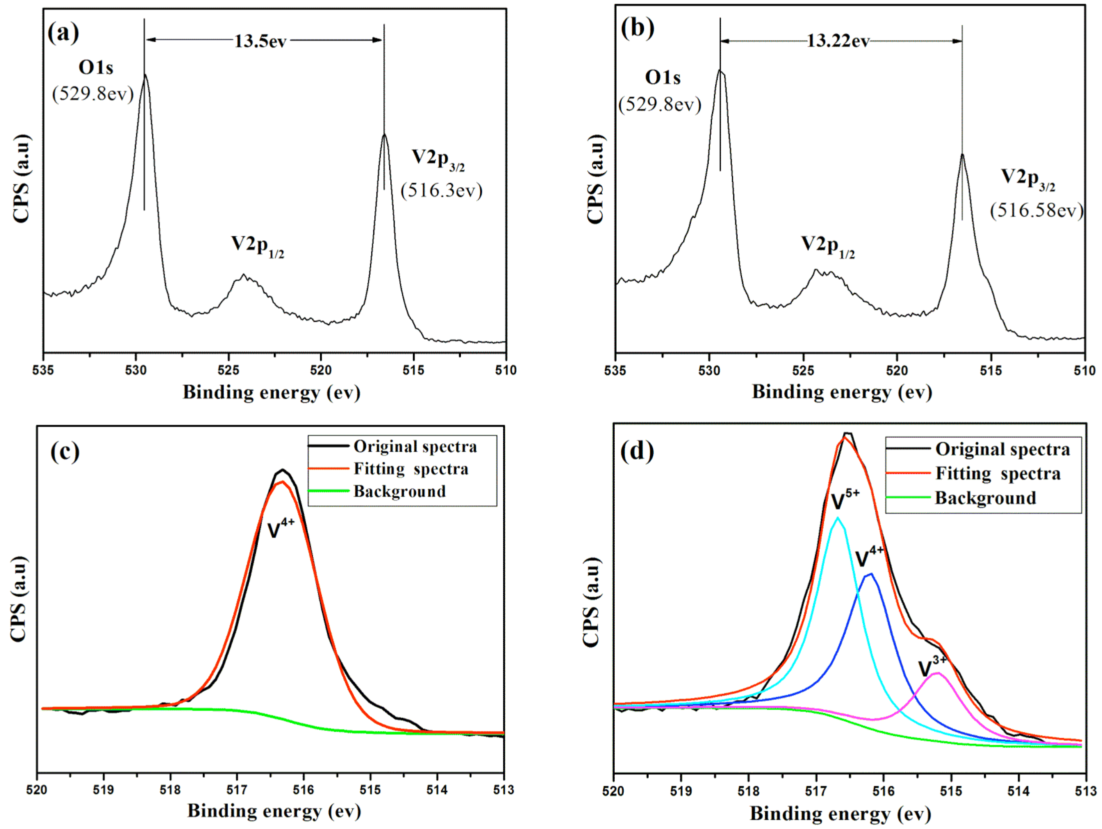

**Figure 4:** The high-resolution XPS spectra of V and O elements for samples without *in-situ* AlN layer (**a**) and with *in-situ* AlN layer (**b**) grown on sapphire substrates by PLD, respectively. The (**c**) and (**d**) are the corresponding fitting results for $V2p_{3/2}$ with XPSPEAK 4.1 softwmare.

529.8eV was taken as reference of internal binding energy. The binding energy (BE) span between O1s and V2p$_{3/2}$ core level could be utilized as a good criterion to judge the valence states of V in VO$_x$ film [14]. As can be seen from Figure **4a** and **b**, the BE spans obtained for samples without and with *in-situ* AlN layer were 13.5 eV and 13.22 eV, respectively. According to Blauw's report in reference, the BE span of 13.5 eV suggests that the main component of sample without *in-situ* AlN layer was VO$_2$, in well agreement with XRD analysis [15]. While the BE span for the sample with *in-situ* AlN layer was smaller than the one obtained from the sample without *in-situ* AlN layer, indicating a higher oxidation state (V$^{5+}$) was included. Moreover, the symmetry characteristics of V2p$_{3/2}$ peak became poor due to the insertion of *in-situ* AlN layer, as shown in Figure **4b**, indicating the *in-situ* layer will induce mixed phases of a number of competing vanadium oxide phases with different vanadium oxidation states such as V$_3$O$_5$, V$_2$O$_3$ or V$_2$O$_5$. The rather good symmetry characteristics of V2p$_{3/2}$ peak in Figure **4a** suggested the pure phase of VO$_2$, even a trace amount of V$^{5+}$ might be removed by Ar+ etching, since it has been confirmed that V$^{5+}$ (derived from surface oxidization either in the annealing process or during storage in air) exist only on the surfaces (the top several nanometers) [13, 16].

In order to further investigate the valence state variation of V in VO$_x$ films induced by *in-situ* AlN layer, the V2p$_{3/2}$ peak was analyzed by XPSPEAK 4.1 software in detail and a Shirley function was used to subtract the background (as shown in Figure **4c** and **d**) [10]. According to the given values in previous report [2,10], the binding energy of 517.2 eV, 516.0 eV and 515.4 eV were attributed to V$^{5+}$, V$^{4+}$ and V$^{3+}$, respectively. The fitting results showed the main valence state of V in the sample without *in-situ* AlN layer was V$^{4+}$, in contrast, the valence state of V become more complicated and VO$_x$ films with the mixed V valence state of V$^{5+}$, V$^{4+}$ and V$^{3+}$ were obtained due to the introduction of AlN interfacial stress layer. It has been reported that the rougher the film surface is, the easier it get oxidized, i.e., more V$^{5+}$ formed [17]. Therefore, these results were in well agreement with that observed in XRD and SEM.

## 3. CONCLUSIONS

The *in-situ* AlN layer induced different crystal structures, components, surface morphologies, and electric properties. It is suggested that the AlN stress layer involved, the bigger film strain induced. The results indicated that for the PLD deposition, the *in-situ* layer will induce a mixed amorphous-like or polycrystalline structures with very fine grains for the vanadium oxide film, as well as mixed phases of a number of competing vanadium oxide phases with different vanadium oxidation states such as V$_3$O$_5$ 、V$_2$O$_3$ or V$_2$O$_5$. The *in-situ* layer also affects the final VO$_2$ films, which needs further investigation. Our achievements will be helpful for understanding the physical mechanism behind the exotic characteristics of VO$_x$ films induced by stress layer. In addition, control of V valence state in VO$_x$ films induced by *in-situ* stress layer makes it more suitable for a wide variety of practical applications.

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