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RESEARCH ARTICLE

Investigation of Optical and Structural Properties of VO_2 Thin Films by Thermal Treatment

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ABSTRACT

In this study, VO_2 thin films were grown on SiO_2 substrate using the PLD method. Then the grown VO_2 thin films were subjected to heat treatments at different temperatures and times in the atmosphere environment. The structural properties of the heat-treated films were investigated using X-ray diffraction (XRD) technique and Raman spectroscopy techniques. The surface microstructures of these films were investigated by Scanning Electron Microscope (SEM) technique, and their optical properties and bond structures were investigated by Photoluminescence (PL) spectra and Fourier Transform Infrared Spectroscopy (FTIR) measurements, respectively. Especially XRD and Raman results revealed that heat treatments with high temperature values transformed the films into VO_2 and V_2O_5 mixed-phase crystal structures. Due to the heat treatment carried out in the atmosphere and the high oxygen affinity of the vanadium metal, crystallization took place in both VO_2 and V_2O_5 forms. In order to obtain homogeneous crystalline VO_2 structures, heat treatments should be carried out for a long time in oxygen-limited environments.

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1. Introduction

Vanadium dioxide; it is an interesting compound that can be found in various polymorphic phases such as VO_2(B), VO_2(A), VO_2(M), VO_2(R), VO_2(P) (Li et al., 2017; Mjejri & Rougier, 2020). In 1959, this compound was shown for the first time by Morin to undergo a very rapid and reversible metal-insulator transition. VO_2 with strong electron affinity can transform from a high-temperature conductive rutile phase VO_2(R) to a low-temperature insulating monoclinic phase VO_2(M) at a critical temperature of 68 ℃. This transition causes radical changes in electrical resistance, optical transmittance and reflection. In addition, physical properties of VO_2 such as electrical conductivity, thermal conductivity and optical transmission can be reversibly and sharply changed by MIT transition with the application of appropriate external stimulus such as photon excitation, heat interaction, electric and magnetic field (Ke et al., 2018; Kumi-Barimah et al., 2020a). These changing physical properties of VO_2 make it a promising candidate for electrical devices such as sensors, memristors, gas sensors, photodetectors and transistors. Particularly, permanent switching of the resistor along the metal insulator transition

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offers an ideal operating mechanism for 2-pole VO_2-based memristor devices (Hou et al., 1991; Hu et al., 2023). Therefore, this transition temperature is very important for technological applications. This transition from the low temperature monoclinic phase to the high temperature rutile phase is accompanied by a structural transition in the compound (Hu et al., 2023). Various factors significantly affect the metal-insulator transition of VO_2 structures operating on the basis of metal-insulator transition. The main of these factors are the thermal stability of VO_2 structures, oxygen defects in the structure, and changes in morphology and crystal structure (Fu et al., 2006; Kim et al., 2016; Rajeswaran et al., 2023). For the development of application-based VO_2 structures, studies in recent years have mostly been done on the thermal treatment behavior of VO_2 thin films. However, these were generally made in vacuum or argon gas environment with very low oxygen pressure, and these environments were quite different from the ordinary atmospheric environment (Fu et al., 2006). In this study, the effect of heat treatment in atmospheric environment on the structural, optical, and morphological properties of VO_2 films was investigated.

2. Materials and Methods

Many methods have been used to produce VO_2 thin films. The main ones of these methods are magnetron sputtering, molecular beam epitaxy, atomic layer deposition, hydrothermal method and pulsed laser deposition (PLD) (Li et al., 2017). Unlike others, the PLD method is ideal for obtaining thin films that are smooth and have the same stoichiometric composition as the target material. Also, its high deposition rate makes it ideal for deposition of oxide films. Therefore, the PLD technique is ideal for oxide thin films (Ke et al., 2019; Kumi-Barimah et al., 2020b). In this study, VO_2 thin films were produced using the PLD method. VO_2 thin films were deposited on (100)-oriented SiO_2 substrates using a KrF (248 nm wavelength) excimer pulsed laser source. A purchased VO_2 target was used as the target material. In the PLD system, distance between target and substrate was kept constant at 24.8 mm. Laser was operated at a power of 350 mJ and it had 10 Hz repetition rate. Laser fluence was adjusted to 2.4 J/cm^2. After films growth, heat treatments were carried out in a closed furnace with atmospheric oxygen inlet. Heat treatments were carried out at 450 and 600 ℃. Heat treatment times were determined as 1 and 3 hours. It was observed that the VO_2 thin films could not adhere to the substrate with higher temperature values and times. Therefore, these high temperature values were not considered in this study. The thickness of the growed VO_2 films was determined by measuring the surface profilometer. Stylus profilometry technique was used as the measurement technique. The bond structures and oxidation states of the films were examined by X-Ray Photoelectron Spectroscopy (XPS) method. XPS measurements were made under Al Kα radiation (hv=1486.6 eV) and using a hemispherical electron analyzer (Phoibos 100, SPECS GmbH). The crystal structures and phase developments of all films were investigated using X-ray diffraction (XRD) technique and Raman spectroscopy techniques. The Rigaku XRD device with CuKα X-ray source (λ = 0.154 nm) was used for XRD measurements. Raman measurements were performed using a device with a nominal power of 340 mW at the output probe and a nominal power of 455 mW at the laser port. A laser with a wavelength of 785 nm was used for Raman measurements. The surface morphologies of the films were examined with the Philips XL 30 SFEG model Scanning Electron Microscope (SEM). We performed Photoluminescence (PL) spectra to investigate the optical activity and oxygen defects of all films. PL measurements were performed with an Agilent Cary Eclipse Fluorescence Spectrophotometer. In addition, analysis and development of bond structures of all films were investigated by performing Fourier Transform Infrared Spectroscopy (FTIR) measurements. All characterization measurements were performed at room temperature.

3. Results

In this study, VO_2 thin films with a thickness of about 100 nm were grown and then were subjected to heat treatments. Figure 1 shows the surface profilometer measurement for a 100 nm thick film.

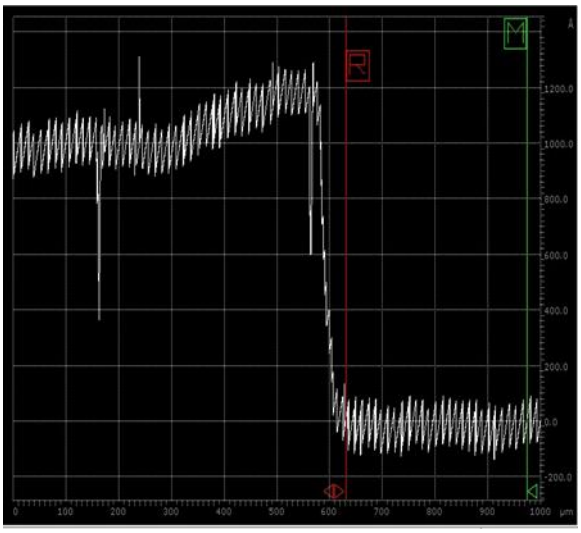

Figure 1. Measurement of film thickness with a surface profilometer.

Figure 2 and 3 show the O 1s and V 2p XPS spectra of VO_2 thin films respectively. When we examine the O and V binding energies from XPS results, the binding energies of O 1s, V $2p_{3/2}$ and V $2p_{1/2}$ were 530.3 eV, 516.5 eV and 523.9 eV respectively. These values are in good agreement with the binding energies of other crystalline VO_2 thin films reported in the literature (Guo et al., 2021a; Martinez et al., 2022). In XPS spectra, it was observed that the V^{4+} vanadium valence state was relatively higher than the V^{5+} valence state of vanadium.

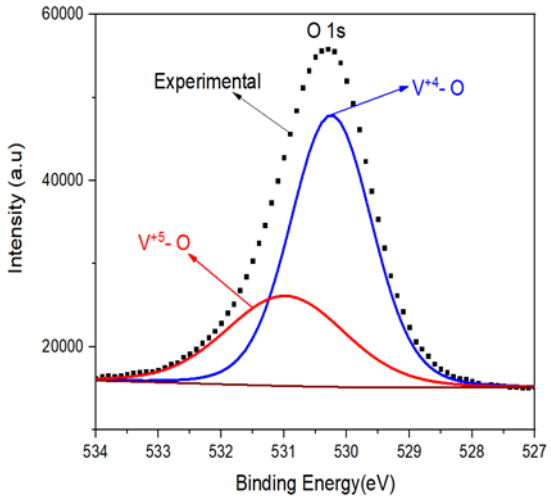

Figure 2. O 1s XPS spectra of VO_2 thin films.

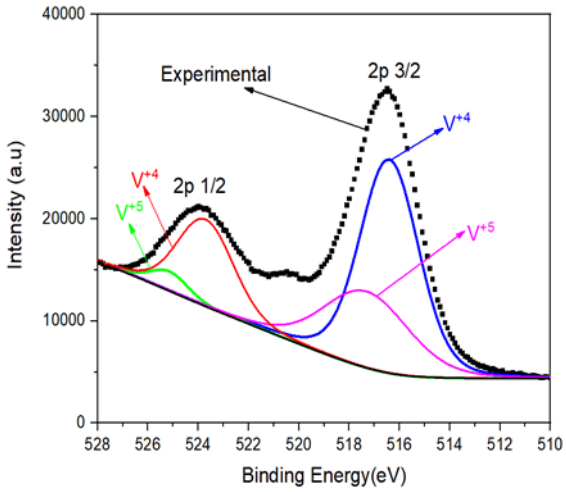

Figure 3. V 2p XPS spectra of VO_2 thin films.

Structural characterizations of approximately 100 nm thick films were made by XRD and Raman measurements. Figure 4 shows the XRD spectra of the as grown and thermally treated films. It was understood that the films that were not thermally treated after growth were amorphous, and they did not have the characteristic VO_2 peak. However, it has been observed that films thermal treated at various temperatures and times form VO_2 or V_2O_5 crystal form. XRD spectra indicates the presence (001), (100) and (210) oriented crystal form of VO_2 at 2θ=15.4°, 18.32°, 42° (Chen et al., 2011; Koza et al., 2011; Huang et al., 2012). Also, spectra indicate the crystal form of V_2O_5 at 2θ=20.3°, 21.7°, 31.06°, 41.2° and 47.3° (Luo et al., 2013; Liu et al., 2016). Peaks at 2θ=33° and 44.34° correspond to SiO_2 substrate and CuKα peak of XRD respectively. XRD results clearly showed that the V_2O_5 form started to form at 450 degrees, but VO_2 began to form at higher temperatures, such as 600 degrees. XRD results clearly showed that at 450 ℃ only V_2O_5 form crystallized, but at 600 ℃ both VO_2 and V_2O_5 form co-crystallized. Therefore, films annealed at 600 degrees were inhomogeneous structures consisting of VO_2 and V_2O_5 crystal structures.

Figure 5 shows the Raman spectra of the as- grown and thermally treated VO_2 films. Raman scattering has characteristic bands at 140.93, 190.99, 280.44, 400.49, 477.55 and 700 cm^{-1}. The bands at 140.93 and 190.99 cm^{-1} are low frequency bands and represent V-V vibrations, while the bands at 400.49 and 477.55 cm^{-1} represent the vibrations of V-O bonds (Prasadam et al., 2019; Guo et al., 2021b). In addition, the bands at 280.44 and 700 cm^{-1} are vibrations originating from the V_2O_5 form (Shvets et al., 2019). Like XRD measurements, Raman measurements clearly reveal that heat-treated VO_2 thin films crystallize in the mixed form of VO_2 and V_2O_5. In addition, bond vibrations were not observed in the thermal treatment performed at low temperature and low annealed time, but characteristic bond vibrations emerged with increasing temperature values and annealed times.

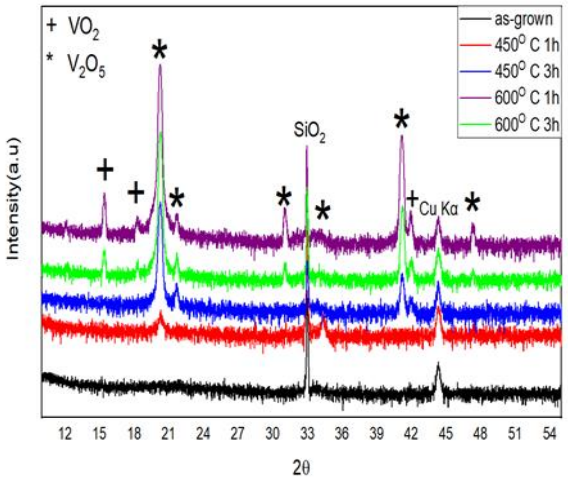

Figure 4. XRD spectra of annealed VO_2 thin films.

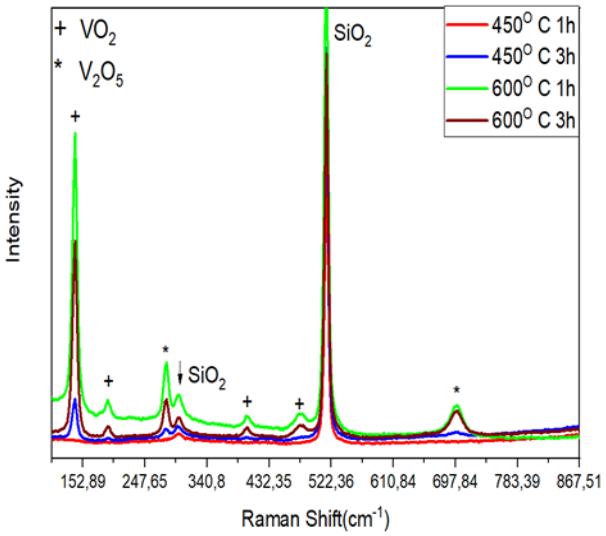

Figure 5. Raman spectra of annealed VO_2 thin films.

Figure 6 shows SEM images of the as grown and thermally treated VO_2 films. It was clearly observed from the SEM images that the heat treatment effect changed the surface microstructures of the VO_2 films. The greatest change occurred in VO_2 films that were thermal treatment at 600 ℃. It was observed that the surface microstructures of films changed with crystallization in proportion to the XRD and Raman results. It was also observed that the agglomerations on the film surfaces disappeared with all heat treatments. But denser surface microstructures were observed at higher temperatures where crystallization occurred. Thermal treatments did not cause any defects on the film surfaces, only this process changed surface microstructures of films.

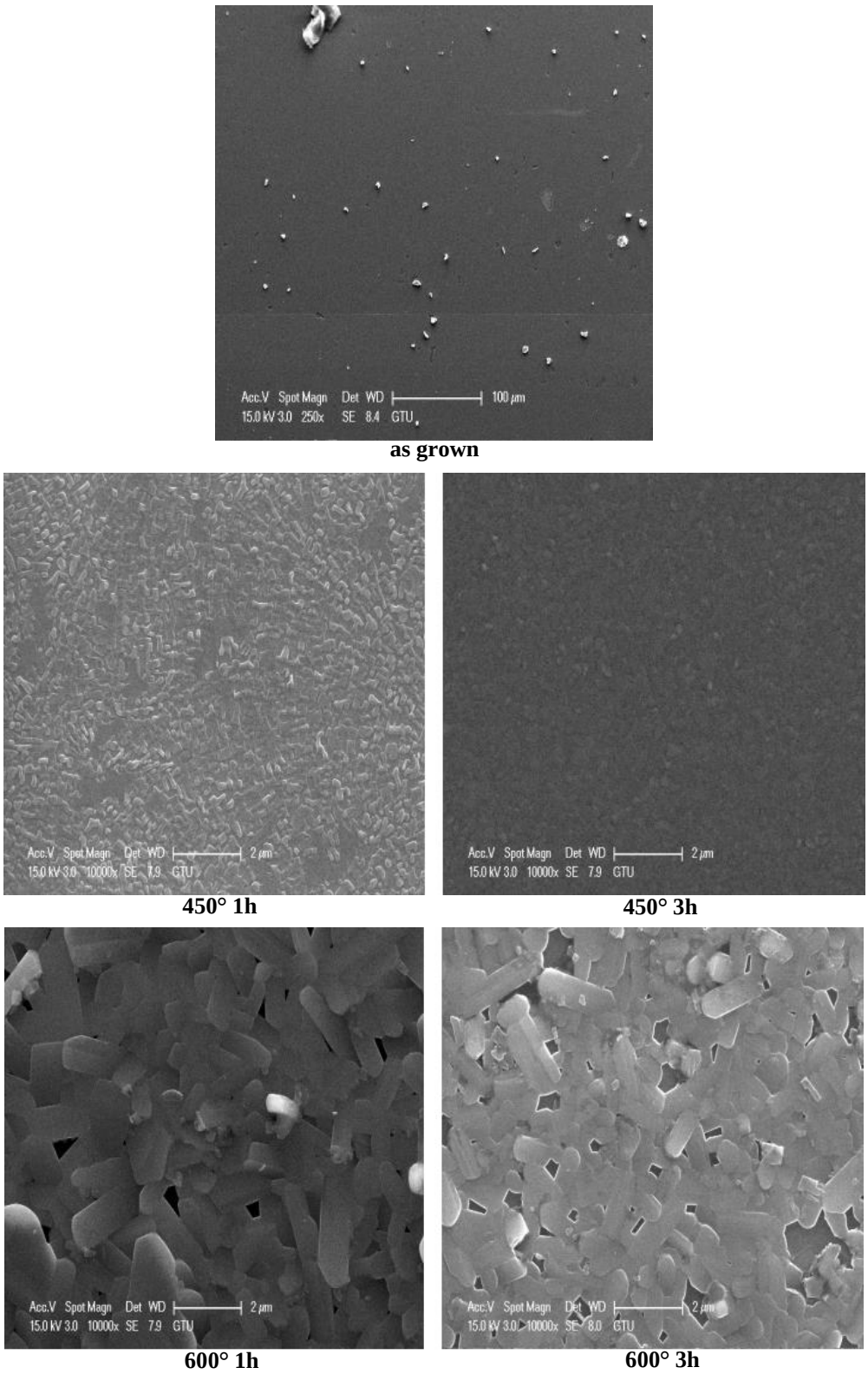

Figure 6. SEM images of the as grown and thermally treated VO_2 films.

Figure 7 indicates PL spectrum of the as- grown and thermal treated VO_2 films. PL spectra usually consist of excitation and emission peaks. Here we focus on emission peaks due to their importance in VO_2-based devices. Because the emission peaks originate from the oxygen vacancies in the structure and these oxygen vacancies play an active role in the operation of VO_2-based devices (Novodvorsky et al., 2018; Joshi et al., 2020). Characteristic emission peaks occurred at about 750 nm of the spectrum. These emission peaks tended to increase with increasing heat treatment temperature and duration. However, it has been observed that longer-term thermal treatments lead to more oxygen defects.

FTIR spectra of as grown and thermal treatment films are given in Figure 8. Quite different characteristic vibrational bands were observed in the spectrum. Vibrations in the range of 480 and 502 cm^{-1} correspond to V-O-V stretching vibrations. According to the condition of the grown film, slip was observed in the bands in this range with the thermal treatment. There are characteristic bands in the spectrum between 608 and 616 cm^{-1}. These are the main vibrational modes in the form of VO_2 and they originate from V- O-V bonds. It was observed that bands in this range appeared with heat treatment. There are also vibrational bands in the spectrum, corresponding to the non-crystalline V-O bond of VO_2. These are the bands between 768 and 785 cm^{-1}. Also, we can see vibrations between 1013 and 1040 cm^{-1} in the spectrum and they correspond to characteristic V=O vibrations of amorphous VO_2. And these have shifted with heat treatment in accordance with the literature (Ji et al., 2017; Zomaya et al., 2020; Li et al., 2022). We can clearly see from FTIR spectra that thermal treatment can change the bond structure of the thin films.

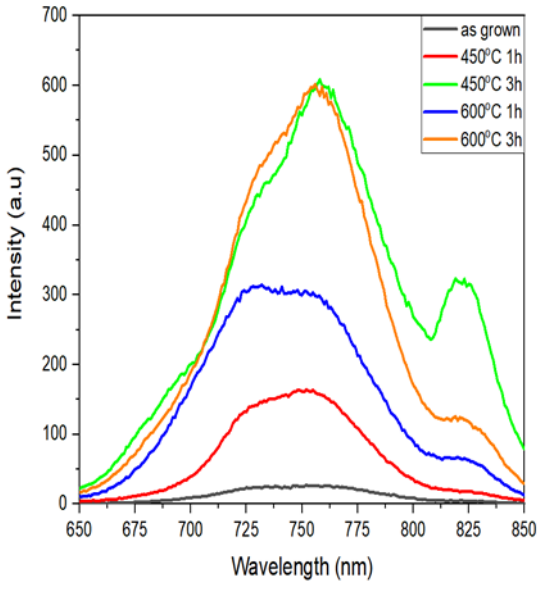

Figure 7. PL spectrum of the as grown and thermally treated VO_2 films.

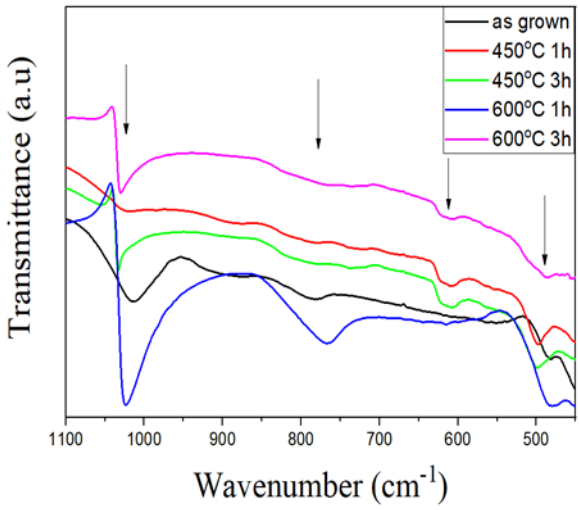

Figure 8. FTIR spectrum of the as grown and thermally treated VO_2 films.

4. Discussion

When we examine the binding energies in XPS measurements, the corresponding binding energies of O and V clearly reveal that the films are formed in the form of VO_2. In addition, the fact that the relative oxidation states of vanadium V^{+4} are higher than V^{+5} indicates that the films have good chemical stability. We understand from the XRD results that amorphous VO_2 thin films can be converted into crystal structures with thermal treatment. However, amorphous VO_2 structures tended to crystallize mostly in the form of V_2O_5 with the heat treatments carried out. As mentioned in the literature, this situation arises from the thermal annealing process carried out in an atmosphere environment or intense oxygen environment. Excessive oxygen affinity of vanadium metal is also effective in this case. To obtain pure crystalline VO_2 structures, annealing should be carried out at high temperatures such as 600 ℃, where oxygen is limited. Like the XRD results, band vibrations representing the characteristic crystalline VO_2 band in Raman measurements could not be obtained by low temperature thermal treatments. Because at low temperature, VO_2 films did not have enough thermal energy to achieve crystallization. Therefore, sufficient activation energy could not be reached to enable the formation of crystalline VO_2 bond structures. By reaching high temperature values such as 600 ℃ or high thermal treatment times the necessary activation energies to provide characteristic bond vibrations of both VO_2 and V_2O_5 have been gained. The high temperatures, where the greatest change in SEM images occurred, indicate amorphous VO_2 films require high thermal energy to crystallize. With the attainment of high temperatures, denser-looking microstructures appeared on the film surfaces. This may be due to the change of the bond structures of the VO_2 film or the crystallization of the structure. The surface microstructures of the films did not have a regular surface appearance at the temperatures where crystallization occurred most. This may be

due to the crystallization of the films in the mixed phase. When we examined the emission peaks in the PL spectra in detail, we saw that there is no major change in the emission peaks caused by oxygen vacancies at longer thermal treatment times. This may be due to the strengthening of bond structures with longer thermal treatment times. In particular, the easy oxidation of the structure resulting from the intense oxygen affinity of vanadium can be shown. Bands in the FTIR spectrum between 608 and 616 cm^{-1} is very interesting. When we interpretted them with XRD and Raman results, these vibrational bands are bands resulting from the crystallization of the film. Because these vibration bands were not found in the as growing film, but they have emerged with thermal treatments. However, other vibration bands in the spectrum are V-O-V and V-O vibration bands in the form of amorphous VO_2 because they were observed in as grown VO_2 film and survived with the heat treatment.

5. Conclusion

XPS results showed that the films grew in the VO_2 form and had good stoichiometric ratios for the VO_2 structure. XRD and Raman results revealed that the growing films were amorphous and transformed into VO_2 and V_2O_5 mixed-phase crystal structures with thermal treatments. There were changes in the surface microstructure of the films with the thermal treatments performed. The largest changes occurred at higher temperatures. Also, we observed from the PL spectrum results that increasing heat treatment temperature and duration caused an increase in the amount of oxygen voids in the film structure. FTIR results showed that in addition to the bands of the amorphous structure of VO_2 films, band structures in crystal form were also formed. We observed from XRD and Raman analyzes that heat treatment can be performed at high temperatures to obtain pure VO_2 crystal structure and bond vibrations, but the amount of oxygen must be limited during the heat treatment. Both XRD and Raman results revealed that VO_2 structures require high energy to transform into a crystalline structure.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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