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Al³⁺ Doped Vanadium Dioxide Thin Films Deposited by PLD

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Abstract

Thin films of vanadium dioxide (VO₂) and Al³⁺ doped VO₂ were deposited on silicon and glass substrates using pulsed laser deposition (PLD). Optimized processing conditions were determined for depositing pure VO₂ with monoclinic phase by laser ablation of a V₂O₅ target. Al³⁺ doping levels in the VO₂ films were varied by altering the relative laser ablation time on the Al₂O₃ and V₂O₅ targets. The change in electrical conductivity with temperature in the semiconductor to metallic phase transition was measured for pure VO₂ and Al³⁺ doped VO₂ films. Doping the VO₂ films with Al³⁺ lowered the transition temperature directly with increasing Al³⁺ content from 67°C for the pure VO₂ films to 40°C at 10% Al³⁺. The magnitude of the resistance change from semiconductor to metallic states also decreased with increasing Al³⁺ doping. The results imply that Al³⁺ doped VO₂ films could be a good candidate for energy efficient “smart window” coatings used for architecture applications.

Keywords: vanadium dioxide, thermochromic, intelligent coatings

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Introduction

Vanadium dioxide (VO_2) undergoes a phase transition from monoclinic structure to tetragonal rutile structure at a transition temperature of 68°C [1-3]. Various ions have been used to dope VO_2 thin films to reduce the transition temperature to near room temperature, for practical use in architectural applications. These applications include “smart windows” that can control the solar radiation through the windows when temperatures increase beyond or decrease below the transition temperature. It was also found that doping with high-valent cations (Nb^{5+} , Mo^{6+} , W^{6+}) lowers the transition temperature, while when doping with low-valent cations (Al^{3+} , Cr^{3+}), the transition temperature is raised [4,5]. An increase of the transition temperature of VO_2 single crystals from 65.5°C to 77°C was found using 1.1 atomic % Al doping, reported as early as 1967 [6]. In another report, Mitsubishi discovered that with the existence of impurities of Al, Fe, and Cr, the VO_2 crystal is stabilized in the triclinic phase instead of the monoclinic phase at low temperatures. Under heating, the triclinic phase transfers to a metastable intermediate phase before it transfers to the tetragonal rutile phase. The first phase transition temperature is lower than the phase transition temperature of pure VO_2 , while the second phase transition is normally higher. The impurities level typically is very low (e.g. hundreds or thousands of ppm). For Al^{3+} doped thin film VO_2 , Lu et al. reported a transition temperature of 72°C for $\text{V}_{0.99}\text{Al}_{0.01}\text{O}_2$ thin films, which is higher than that of pure VO_2 thin films (i.e. 67°C) [7]. In all the reports above, the Al^{3+} doping level is relatively low to ensure that VO_2 maintains its crystal structure framework integrity so that the phase transition with temperature does not disappear. In contrast to the previous reports, recently Gentle et al. [8] found that the transition temperatures of Al doped VO_2 decrease with an increase in Al-doping levels (see Figures 2 and 3 of ref. 8). However, the

Al % in the VO₂ was not provided as the study focused on the electrical behavior of doped VO₂ below or above the transition temperatures.

In an attempt to raise the transition temperature of VO₂ films for switchable solar thermal absorber applications, we have used pulsed laser deposition (PLD) to ablate a composite VO₂/Al₂O₃ target to deposit Al⁺³ doped VO₂ thin films. It was found that the transition temperatures of Al⁺³ doped VO₂ films decreased instead of increasing, in contrast to the majority of previous reports. If Al⁺³ doped VO₂ film indeed could reduce the transition temperatures to near room temperature, it would be an excellent candidate as an energy efficient “smart window” coating used for architectural applications. In comparison with pure VO₂ films, Al⁺³ doped VO₂ films such as V_{0.99}Al_{0.01}O₂ exhibit a higher optical transmittance at temperatures before and after the phase transition which is better than pure VO₂ for “smart window” applications [7].

This work presents the optimized processing parameters developed for the PLD method to produce pure VO₂ phase from a V₂O₅ target. The Al⁺³ doped VO₂ films were produced under the same processing parameters as those for pure VO₂ films by subsequent ablation of a VO₂ and Al₂O₃ target. The crystal structure of the doped and un-doped VO₂ films was investigated using XRD, while the electrical properties during heating and cooling of the films was examined using the four-point probe technique. The Al⁺³ doping levels were varied to examine this effect on the transition temperature as well as on the electrical resistivity.

Experimental Details

For the deposition experiments, a pulsed laser beam generated by a KrF excimer laser at a wavelength of 248 nm and pulse duration of 25 ns was introduced into the deposition chamber through a quartz window, and focused using an optical lens onto the target surface. The laser fluence on the target was 2~3 J/cm², while the repetition rate was fixed at 50 Hz. For the deposition of pure VO₂ films, a 3-inch circular vanadium pentoxide (V₂O₅) target was used for the laser ablation. For the deposition of Al⁺³ doped VO₂ films, a 3-inch circular aluminum oxide (Al₂O₃) target was cut into pie-shaped sectors with different angles, then one Al₂O₃ or WO₃ target sector of selected angle was mounted on the top of the 3-inch circular vanadium pentoxide target. The laser beam was subsequently ablated on the rotating Al₂O₃/V₂O₅ target surface to deposit composite films. The pure V₂O₅ or Al₂O₃/V₂O₅ target was rotated at a speed of 18 rpm. Thin films were deposited directly on either 3-inch diameter (100) oriented silicon wafers or 18 mm x 18 mm x 1.5 mm soda lime glass substrates. To improve the film homogeneities, the substrates were rotated along the vertical axis at a speed of 35 rpm. Films were deposited at temperatures ranging from 400°C to 600°C, and under high vacuum or with oxygen process gas at pressures ranging from 1 to 50 mtorr.

The surface morphology of the films was analyzed by a Leo 440 field emission scanning electron microscope (FE-SEM), while the crystallographic properties of the thin films were analyzed by X-ray diffraction (XRD, Philips, X-Pert MRD) using monochromatized Cu K_α in the θ_0 -2 θ thin film configuration, where θ_0 was fixed at 0.5°. The diffraction photons were collected by the diffractometer from 20-70° with a 0.02° step size. The chemical states and compositions of the

films were investigated by x-ray photoelectron spectroscopy (XPS). The XPS measurements were performed using a Kratos Axis Ultra spectrometer equipped with an $AlK\alpha$ source ($\lambda = 1486.6$ eV). The resistances of the films were studied by a four-point probe setup. Four-point probe measurements were carried out using a 4 point probe head (SP4-62085TRS, from Lucas Signatone Corporation) with Tenma's DC power supply (72-6615) and a National Instrument's DAQ card. Data acquisition was implemented by a LabView program which automatically acquired the current, voltage and temperature. The heating and cooling rate for the 4 point resistance measurement are approximately 10 °C/minute for the heating and 1 °C/minute for the cooling. The sheet resistance (R_s) of films was calculated using the equation: $R_s = 4.53 V / I$, as the thickness of thin vanadium oxide films (~ 300 nm) is much smaller than the probe distance.

Results and Discussion

XRD patterns of Vanadium oxide films deposited onto silicon (100) wafers at 600 °C in vacuum and in oxygen pressures of 1.4, 6.1 and 47 mTorr, respectively, are shown in Figure 1. In vacuum, laser ablation of V_2O_5 produced mixed phases of Vanadium oxides that could include phases such as V_3O_5 or V_2O_3 with oxidation states of vanadium lower than +4. Due to the broadness and ill-defined features of these XRD peaks, assignment of any individual peak to a particular phase is difficult. However, when deposition occurred using 1.4 to 6.1 mTorr of O_2 , a very well-defined XRD pattern appeared corresponding to the monoclinic VO_2 phase. All the peaks observed in the XRD patterns have been attributed to their corresponding VO_2 index planes (ICDD file 44-0252). No additional peaks due to other vanadium oxide phases are observed from the patterns, indicating the phase purity of these films. The VO_2 films deposited in this O_2 pressure range are preferentially oriented in the (011) plane as the main diffraction

peak at $2\theta = 28.3^\circ$ is the Bragg reflection from the (0 1 1) lattice planes. When deposition occurred using 47 mTorr of O_2 , pure orthorhombic V_2O_5 phase was produced. The main diffraction peak at $2\theta = 20.3^\circ$ is attributed to the Bragg reflection from the (0 0 1) lattice planes of the orthorhombic V_2O_5 , suggesting that the texture of laser-ablated thin films is oriented along the c-axis perpendicular to the surface of the silicon substrate with a, b axes parallel to the surfaces [9, 10]. The two small peaks appearing at $2\theta = 12.3^\circ$ and 21.8° are attributed to the Bragg reflection from the (200) plane of tetragonal V_2O_5 and the (101) plane of orthorhombic V_2O_5 , respectively. The XRD results in Figure 1 clearly show that at 600°C , optimized oxygen pressures for growing pure VO_2 films by PLD is 1.4 to 6.1 mTorr.

Figure 2 shows the XRD patterns of Vanadium oxide films deposited using 1.4 mTorr O_2 at 400, 500, and 600°C , respectively. For films deposited at 400°C , the diffraction patterns consist of a few weak diffraction peaks at $2\theta = 14.5^\circ$, 29.0° and 44.5° overlapped over a diffuse-scattering curve with a broad band centered at 2θ of about 27° . Such a profile indicates a mixed amorphous-like and polycrystalline structure or polycrystalline structures with very fine grains for the Vanadium oxide film. The weak diffraction peaks can be assigned to Bragg reflection from the (001), (110) and (210) planes of monoclinic VO_2 phase. At the deposition temperature of 500°C , a pattern corresponding to the polycrystalline monoclinic VO_2 phase clearly appears. All the peaks observed in these XRD patterns have also been attributed to their corresponding VO_2 state (ICDD file 44-0252) and the main diffraction peaks are indexed in figure 2. At 600°C , VO_2 films are preferentially oriented along the c-axis perpendicular to the surface of the silicon substrate in the (011) plane. Results in figure 2 indicate that Vanadium oxide films deposited at low O_2 pressure (e.g. 1.4 mTorr) began to crystallize at 400°C , and at 600°C a textured

monoclinic VO₂ phase was grown. From the results in figures 1 and 2, the optimized processing parameters selected for the deposition of Al³⁺ doped VO₂ films was determined to be 1.4 to 6.1 mTorr at 600°C.

For the deposition of Al³⁺ doped VO₂ films, the KrF laser beam was subsequently ablated on the rotating Al₂O₃/V₂O₅ target surface in 1.4 mTorr of O₂ gas. A 3-inch circular silicon wafer or a 18 mm x 18 mm x 1.5 mm soda lime glass substrate heated up to 600°C was used as the substrate to collect the laser plume to grow the doped VO₂ films. Various Al³⁺ doping contents in VO₂ films were obtained by using different angles of the pie-shaped Al₂O₃ target sitting on top of the circular V₂O₅ target for the laser ablation. Figure 3 shows the XRD patterns of the pure VO₂ film and the VO₂ films obtained at increasing angles of the Al₂O₃ target to increase the level of Al³⁺ doping. The XRD patterns of doped and un-doped VO₂ films are similar in terms of the number of peaks and peak locations indicating that doping of Al³⁺ ions into VO₂ films does not alter the monoclinic crystal structure and lattice constants of VO₂ films. However, doping does decrease the grain size as the intensity of diffraction peaks decreases and their FWHM increases with the Al³⁺ doping. No diffraction peaks due to Al₂O₃ appeared, indicating that Al³⁺ ions were dispersed uniformly into the VO₂ lattices. The microstructural change with Al³⁺ doping films can also be examined by FE-SEM as shown in Figure 4. The grain size of Al³⁺ doped VO₂ films, which is around 40 nm, is significantly smaller than that of the pure VO₂ film (~ 80nm). The grain size did not show a significant change with the various doping levels. This is consistent with the XRD results in Figure 3 where the XRD peak intensity does not vary significantly with doping levels.

The chemical composition of the Al^{3+} doped VO_2 films with varying Al^{3+} contents were investigated by XPS measurements. From the intensities of the $\text{Al}2p$ and $\text{V}2p$ peaks of the XPS spectra, and by taking into account the specific sensitivity factors of the two elements, we calculated the atomic percentage ratios of Al and V for the doped films. The Al/V atomic percentage ratios were determined to be 4.9% ($5^\circ \text{Al}_2\text{O}_3$ doped film), 6.1% ($10^\circ \text{Al}_2\text{O}_3$ doped film), and 10% ($25^\circ \text{Al}_2\text{O}_3$ doped film) respectively. High resolution XPS spectra for $\text{V}2p$ core levels of the three films are shown in Figure 5, in which the background due to the Al $K\alpha$ radiation was subtracted from the spectra. The $\text{V}2p$ region of all films exhibited two primary peaks at around 523.7 and 516.3 eV, which correspond to the $\text{V}2p_{1/2}$ and $\text{V}2p_{3/2}$ core levels, respectively. The primary peaks' location in the three films are slightly different (within 0.13 eV), while the splitting energy between the $\text{V}2p_{1/2}$ and $\text{V}2p_{3/2}$ levels is similar for all 3 samples, i.e. 7.4 eV. In addition, there are small detectable peaks located at 517.8 eV for films, which correspond to the $\text{V}2p_{3/2}$ core level spectrum for V^{5+} . The large peaks around 532 eV correspond to $\text{O}1s$.

The influence of Al^{3+} doping on the electrical properties of the VO_2 films deposited at 600°C in 1.4 mTorr of O_2 on soda lime glass substrates was studied by measuring their sheet resistance using the conventional four point probe method, with the results shown in Figure 6. For the pure VO_2 film, the semiconductor-metal transition occurs at a temperature of about 67°C and shows 2.5 orders of magnitude difference in resistance measurement between the two states. The profile reveals a smooth transition, both in heating and cooling, and displays a temperature hysteresis of about 15°C . The corresponding resistance-temperature profiles for the various Al^{3+} doping levels are also given in Figure 5, showing the effect of Al^{3+} doping on the phase transition

temperatures. The transition temperatures lower as the doping level increased, decreasing about 20 ~ 30 °C. The presence of Al^{3+} ions immediately narrowed the hysteresis loop by about half to approximately 7 °C. The magnitude of the resistance changes across the transition decreased from 2.5 orders of magnitude for the pure VO_2 film to 1.6 orders of magnitude for the Al^{3+} doped films. The resistance of Al^{3+} doped VO_2 films is much lower than pure VO_2 film and the higher the doping level, the lower the resistance.

Doping of VO_2 with low-valent cations was reported to increase the semiconductor-metal phase transition temperatures in the majority of the previous literature [6, 7]. The increase in transition temperatures when doping with low-valent cations was explained as the result of lattice distortion when smaller size low-valent cations substitute larger size V^{4+} ion in a homopolarbonding V^{4+} - V^{4+} pair. The substitution distorts the monoclinic lattice towards the triclinic lattice, and the increment of distortion energy raises the transition temperature [6]. In this paper, the XRD results of PLD deposited Al^{3+} doping VO_2 films in figure 3 does not show any noticeable lattice distortion as the XRD peaks position does not shift with Al^{3+} doping, and does not change with doping level. However, the peak intensity decreases significantly with Al^{3+} doping, indicating that the grain/particle size is decreasing. Microstructural changes after Al^{3+} doping in VO_2 could be one of the factors that determined both the magnitude of the bandwidth and the onset temperature of the phase transition [11]. In addition, crystalline defects due to oxygen vacancy on the particle surface induced by Al^{3+} doping could also become a dominant factor determining the crystalline properties and the phase transition temperature [12]. However, since Al^{3+} doping in VO_2 films with such a high magnitude as utilized in this work has not been

reported previously, the mechanism that causes the decrease in the phase transition temperatures needs more careful investigation.

Conclusions

In conclusion, the pure VO₂ and Al³⁺ doped VO₂ thin films were grown by the PLD technique on Si and soda lime glass substrates at optimized processing conditions of 1.4 mtorr O₂ process gas and 600 °C substrate temperatures. The content of Al³⁺ in the doped films was varied by altering the relative laser ablation time on the Al₂O₃ and V₂O₅ targets using various angles of pie-shaped Al₂O₃ target sectors. The electrical resistance measured upon heating and cooling of the PLD films shows the semiconductor-metal transition at temperatures of around 67 °C for pure VO₂ films, while for Al³⁺ doped VO₂ films the transition temperature decreases to as low as 40°C. The magnitude of the resistance change from the semiconductor to metallic states also decreased with Al³⁺ doping. The hysteresis loop was narrower for the Al³⁺ doped films compared to the broad hysteresis of the pure VO₂ film on glass. These results imply that Al³⁺ doped VO₂ films could be a good candidate as energy efficient “smart window” coatings for architecture applications.

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Figure Captions:

Figure 1: XRD spectra of Vanadium oxide films deposited at the substrate temperature of 600 °C on silicon (100) substrates in vacuum (a) and in O₂ pressure of 1.4 mTorr (b), 6.1 mTorr (C), and 47 mTorr (d).

Figure 2: XRD spectra of Vanadium oxide films deposited at the substrate temperature of 600 °C (a), 500°C (b), and 400 °C (c) on silicon (100) substrates in O₂ pressure of 1.47 mTorr.

Figure 3: XRD spectra of Vanadium dioxide films deposited at the substrate temperature of 600 °C in O₂ pressure of 1.47 mTorr with various Al³⁺ doping levels.

Figure 4: FESEM topography images of Vanadium dioxide films deposited by PLD. (a) Pure VO₂ film, (b) 5° Al₂O₃ doped VO₂ film, (c) 10° Al₂O₃ doped VO₂ film, and (c) 25° Al₂O₃ doped VO₂ films.

Figure 5: High resolution XPS spectra of Al₂O₃ doped VO₂ films on (100) Silicon substrates.

Figure 6: Temperature dependence of sheet resistance of the pure VO₂ films and Al³⁺ doped VO₂ films on glass substrates.

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Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6