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Study of Si doped VO₂ thin films for solar thermal applications

A. Krammer^{a,*}, O. Bouvard^a, A. Schüler^a

^a Solar Energy and Building Physics Laboratory (LESO-PB), Ecole Polytechnique Federale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

Abstract

A new generation of smart solar thermal collectors is based on thermochromic thin film technology. Thermochromic absorber coatings change their optical properties with temperature, particularly in the infrared range. In order to prevent overheating, the collector selectivity is deliberately hindered, through an increase of the thermal emittance above a critical temperature. The transition temperature of pure thermochromic VO₂ (68°C) needs to be adjusted for solar thermal applications and to do that Si doping is attempted. Thus, pure and Si doped vanadium dioxide thin films are deposited by reactive magnetron sputtering and the films are characterized by four point probe and in-situ X-ray and UV photoelectron spectroscopic measurements. While a modest increase in the transition temperature with doping is reached (up to a critical Si concentration when the transition is lost), the insulating character of the films is also enhanced (decreased density of states at the Fermi level).

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1. Introduction

Despite being one of the most established and common solar energy harvesting systems in use today, until recently, solar thermal collectors for domestic hot water generation faced the problem of overheating. During cold periods all absorbed energy is useful. However, during hot periods, when solar radiation is abundant and demand is low, stagnation occurs. Excess heat cannot be diverted and collector temperatures can exceed 200°C even in central European latitudes. The heat transfer fluid evaporates, glycols degrade, while frame, insulation and absorber coating are damaged and become less efficient. Self-draining systems or mechanical shading solutions complicate

*Corresponding author. *Email address:* anna.krammer@epfl.ch

construction and add to the system costs.

A novel way of preventing overheating of solar thermal collectors has been proposed [1,2]. The innovative approach is based on switchable multilayered absorber coatings where the smart function comes from the integration of thermochromic vanadium dioxide thin films. VO₂ has long been at the forefront of research due to its fast and reversible semiconductor-to-metal transition (SMT) which is marked by abrupt optical changes in the infrared range. Absorbers with good selectivity below and bad selectivity above the transition temperature are developed by exploiting the sudden change in thermal emittance upon transition from ~5% below T_C to ~35-40% above T_C. Then, above the critical temperature in the high emissivity state, the collector radiates the heat off to the surroundings, thus limiting the stagnation temperature below the evaporation temperature of the transfer fluid. The first such thermochromic collector has recently become commercially available [3].

Pure vanadium dioxide switches at 68°C and this proximity to room temperature lead to considerable interest in a plethora of applications such as smart windows [4], steep-slope electronic switches [5], tunable capacitors [6], etc. However, for highly efficient solar collectors as considered in the present work, the optimization of the transition temperature from 68°C to above 90°C (just below the boiling temperature of water) is required.

Doping is known to alter the temperature at which the first order phase transition occurs. Most studies have been carried out on dopants decreasing the transition temperature, up to date W-doping proving the most successful. Dopants increasing the transition temperature were scarcely considered. In this work, the potential of Si doping in raising the transition temperature is determined. Its effect on VO₂ valence band and core-level spectra is also studied.

2. Experimental methods

2.1. Film deposition

Pure and Si doped switching vanadium dioxide films are deposited by reactive magnetron co-sputtering on <100> Si substrates. The thickness of the deposited films is ~320 nm. The deposition is carried out at 600°C (measured by a stationary thermocouple above the rotating substrate holder). The magnetrons are run by DC power for the vanadium target and by radio frequency (RF) AC power for the silicon target. The purity of the 2" target discs is guaranteed at 99.95% for the V and 99.999% for the Si target. 150 W power is applied on the V target, while the power on the Si target is changed between 0 and 25W in order to vary the Si content of the deposited films. To further limit the Si doping, some magnets are removed from the magnetron with the Si target, thus reducing the magnetic field and subsequently the plasma density.

The base pressure of the chamber is kept below $3 \cdot 10^{-7}$ mbar. Ar (99.999% purity) – process gas and O₂ (99.995% purity) – reactive gas are introduced in the chamber. The Ar flow, controlled by a mass flow controller, is set to 17.4 sccm. The oxygen partial pressure is kept constant by a Proportional Integral Derivative (PID) feedback control which regulates the oxygen flux based on the pressure readings of an oxygen sensor (lambda sensor Zirox XS22). During depositions, the oxygen partial pressure is in the range of $6 \pm 0.25 \cdot 10^{-4}$ mbar. The working pressure is $\sim 6 \cdot 10^{-3}$ mbar.

2.2. Film characterization

The films are characterized by *in-situ* X-ray (XPS) and ultraviolet (UPS) photoelectron spectroscopy (SPECS Leybold EA11 MCD electron spectrometer). The high-vacuum deposition chamber is connected to the UHV ultraviolet and X-ray photoelectron spectrometer, the samples being transferred from one system to another without breaking the vacuum. Hence, sample contamination is avoided and no sputter cleaning is needed.

The base pressure in the measurement chamber, even without liquid nitrogen cooling, is in the range of $5 \cdot 10^{-10}$ mbar. The spectrometer is equipped with a He discharge lamp for UPS (He I at $h\nu = 21.22$ eV, He II at $h\nu = 40.82$ eV) and an X-ray source for the XPS (Mg K α at $h\nu = 1253.6$ eV) measurement. The XPS core level spectra are measured at 29.925 eV pass energy. For the electron energy calibration, the Au 4f_{7/2} core-level signal at 83.8 eV binding energy is taken as reference.

The temperature dependent electrical resistivity of the films, from room temperature to 95°C, is determined by standard four-point probe measurement in the Van der Pauw configuration.

3. Results and discussion

Five vanadium oxide based samples, with varying composition, have been deposited. The Si content of the films is changed by adjusting the applied power on the Si target. Higher applied power corresponds to higher concentration of dopant element in the deposited film. The samples are summarized in Table 1.

Table 1. List of deposited samples and corresponding applied power on the Si target.

| Sample | S1 | S2 | S3 | S4 | S5 |
|------------------------------------|----|----|----|----|----|
| Power applied on the Si target [W] | 0 | 8 | 15 | 20 | 25 |

3.1. Four-point resistivity measurements

The temperature dependent electrical resistivity of the thin films is shown in Figure 1 and the influence of Si doping on the thermochromic properties is investigated. In order to precisely determine the phase transition temperature for the heating, T_h and cooling, T_c cycles, hysteresis widths and the sharpness of the transition, the first derivative of the resistivity against temperature is fitted with Gaussian functions and plotted for each sample.

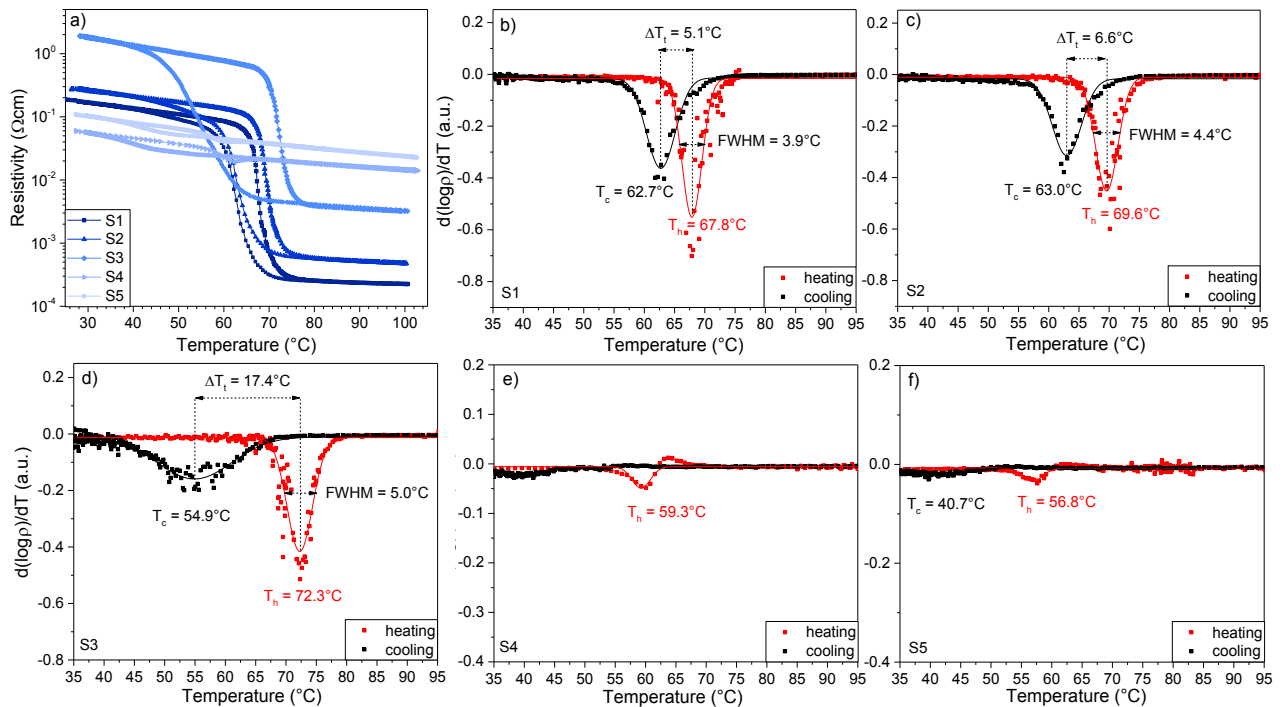


Figure 1. a) Temperature dependent resistivity curves of pure and Si doped VO_2 films. The $d(\log\rho)/dT$ vs T plots for pure VO_2 (b) and $\text{V}_{(1-x)}\text{Si}_x\text{O}_2$ films with 8W (c), 15W(d), 20W (e), 25W (f) power applied on the Si target. Symbols denote measured data points, fitted with Gaussian functions. The minima indicate the transition temperature during heating, T_h and cooling, T_c . The difference between the two is the hysteresis width ΔT_i . The FWHM gives the sharpness of the transition.

The minima are then defined as the transition temperature (during the heating and cooling cycles), the difference between T_h and T_c as the hysteresis width ΔT_i and the full width at half maximum (FWHM) gives an indication on the steepness of the transition.

The pure VO_2 film switches at 67.8°C during heating. The transition temperature, the hysteresis width and the resistivity values in both cold and hot state increase gradually with doping up to a certain point, between 1.2 and 1.5 at.% Si, when film amorphization is induced and the switching character of the films is lost.

3.2. UV photoelectron spectroscopy

After the deposition, three samples: VO_2 , $\text{V}_{0.988}\text{Si}_{0.012}\text{O}_2$ and $\text{V}_{0.985}\text{Si}_{0.015}\text{O}_2$ are immediately transferred to the photoelectron spectrometer while still in the hot state. UPS He I spectra are measured continuously during sample cooling in order to observe the metal-to-semiconductor transition and its effects on the density of states at the Fermi level. Once the valence band edge does not shift and the sample reached its low temperature state, UPS He II spectra are measured too.

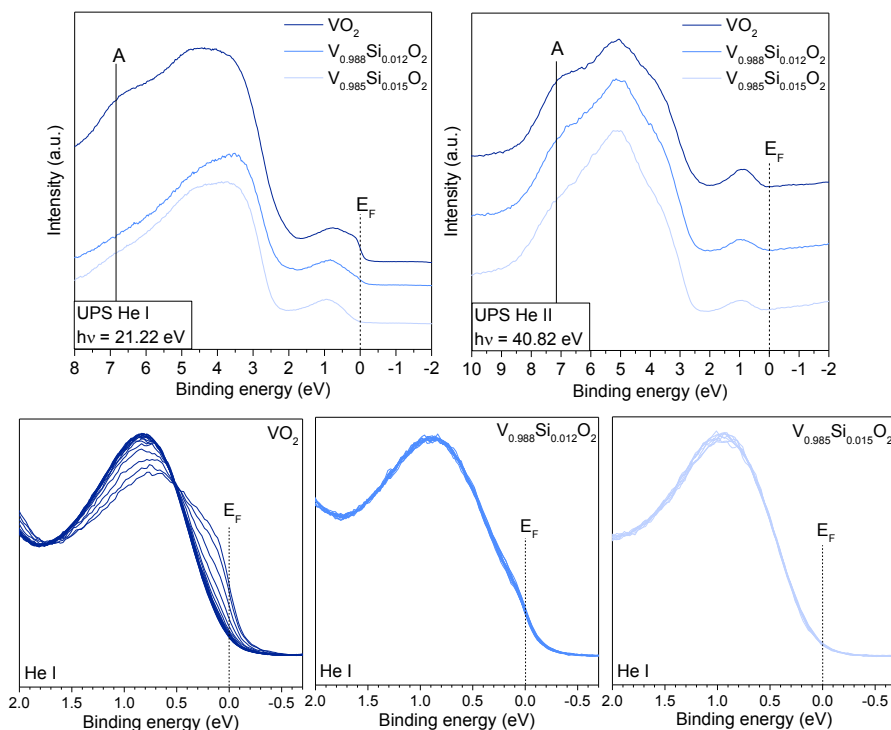


Figure 2. He I and He II valence band spectra of pure VO_2 and doped $\text{V}_{(1-x)}\text{Si}_x\text{O}_2$ films. A zoomed in view of the He I spectra near the Fermi level is given for all three samples. The dashed and solid straight lines mark the position of the Fermi edge and the bonding O $2p\sigma$ orbitals with the V d band respectively.

In Figure 2, the He I spectra of the pure and Si doped VO_2 films, with 1.2 and 1.5 at.% Si content, is shown. For better legibility, a zoomed view of the Fermi level during the cooling process is displayed for each sample. A decrease of the density of states at the Fermi level, associated with V 3d states, is observed with Si doping. For the pure VO_2 film, the opening of a band gap during cooling marks the in-situ metal-insulator transition. For the sample with 1.2 at.% Si only a vague Fermi edge is detectable while changes in the density of states with cooling are moderate. Sample $\text{V}_{0.985}\text{Si}_{0.015}\text{O}_2$ behaves as a semiconducting sample in both hot and cold states with essentially no noticeable changes to the valence band edge with temperature. In both the He I and II spectra, broad shoulder-like features centred around 4.8 and 7 eV binding energies are identified. According to [7], these two bands at 4.8 and 7 eV are related to non-bonding O $2p\pi$ and bonding O $2p\sigma$ orbitals with V d band. The intensity of the feature at 7 eV binding energy, indicated in the figure with the solid black line labelled “A”, is changing with Si doping. This suggests that Si reduces the strong V 3d–O $2p\sigma$ band hybridization.

3.3. X-ray photoelectron spectroscopy

XPS was used to determine the chemical composition of the deposited films. Elemental quantification was based on the O1s, V2p_{3/2} and Si2p core-level peak integration, using Scofield sensitivity factors combined with calibration with pure VO₂ sample. A Shirley background was adopted. As expected, for the pure VO₂ sample no Si peaks were identified. For the two doped samples, the quantification yielded 1.2 and 1.5at.% Si content, respectively. The ratio between the at.% of V and O was 1:2 for the pure sample and 1:2.05 for the two doped samples.

In Figure 3 the O1s and V2p core level spectra of the VO₂, V_{0.988}Si_{0.012}O₂ and V_{0.985}Si_{0.015}O₂ samples are shown. The spin-orbit splitting leads to the two-peak vanadium structure, 2p_{1/2} and 2p_{3/2}. The core lines appear to shift to higher binding energies with Si doping.

Broad V2p_{3/2} lines are observed. This is consistent with literature where reported FWHM values of the 2p_{3/2} peaks range widely from 1.95 to 3.2 eV and have been explained by various multiplet configurations in the photoemission final states, resulting from core-hole - 3d electrons interaction [8-9]. Besides broadening, this core-hole – 3d electron coupling also results in satellite structures falling in the high-binding energy side of the O1s peak and leading to the asymmetry around ~531eV [10].

The V2p_{3/2} peak deconvolution resulted in two components, P1 and P2, fitted with mixed Lorentzian-Gaussian curves. Peaking at ~515.7 and ~517 eV respectively, the two components coincide with the reported binding energies of the V⁴⁺ and V⁵⁺ 2p_{3/2} core lines. Indeed, we attribute component P1 to the V⁴⁺ states as both its peak position and FWHM of ~1.9 – 2.2 eV closely match those reported for V2p_{3/2} core lines of highly pure VO₂ samples. As VO₂ surfaces readily over-oxidize into V₂O₅, it is also likely that a fair amount of V⁵⁺ oxide is present. However, for P2 to be attributed solely to the V⁵⁺ contribution, it is striking that rather small amounts of Si induce such stark changes in the P1:P2 ratio, especially when the V:O ratio is basically unchanged (1:2). Furthermore, at 2.2 – 2.3 eV, the FWHM of the P2 component is broader than those reported for V⁵⁺.

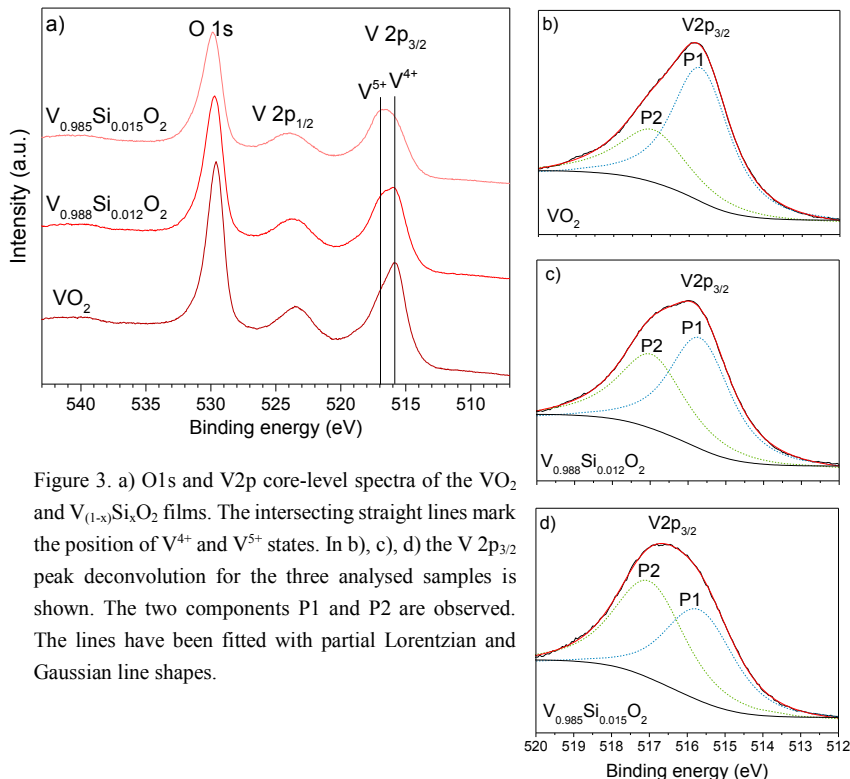


Figure 3. a) O1s and V2p core-level spectra of the VO₂ and V_(1-x)Si_xO₂ films. The intersecting straight lines mark the position of V⁴⁺ and V⁵⁺ states. In b), c), d) the V 2p_{3/2} peak deconvolution for the three analysed samples is shown. The two components P1 and P2 are observed. The lines have been fitted with partial Lorentzian and Gaussian line shapes.

2p spectra of first row transition metals are challenging to interpret due to peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structures and uncertain, overlapping binding energies. [11] In Ti-Al-N films, complex Ti2p line shapes have been reported [12]. The authors interpret this in terms of a well screened main doublet

and a poorly screened satellite doublet, which becomes dominant as the screening ability of conduction electrons is decreasing with Al content. Fine structured $2p_{3/2}$ core lines were also reported for NiO and Cu based materials and have been explained based on non-local screening effects. This means that an electron could be taken from a far oxygen atom and transferred to the photoionized site. [13] Therefore, it is possible that various satellite structures might be present in the higher binding energy side of the $V2p_{3/2}$ peaks as well. Small Si doping appears to significantly strengthen the P2 component which could be an indication of some non-local screening effects.

4. Conclusions

Pure and Si doped vanadium dioxide films have been reactively sputtered on Si substrates and studied by four-point probe resistivity measurements, UPS and XPS. From the temperature dependent resistivity curves it is shown that Si doping raises the metal-insulator transition temperature (increase of $\sim 4.5^\circ\text{C}$ reached). Moreover, film amorphization is induced early by doping and, already above 1.2at% Si content, the transition is lost. The resistivity values continue to increase with doping over the measured temperature range.

Through doping, the metallic character of the films in the hot state is hindered in favour of an insulating behaviour. From the UPS spectra it is shown that the density of states at the Fermi level decreases with doping and at 1.5 at% Si a band gap has opened up.

In XPS, the $V2p_{3/2}$ peak deconvolution shows that fitted components peak at 515.7eV and 517eV binding energy. The former is associated with V^{4+} states, while for the origin of the latter V^{5+} states, shake up and non-local screening satellites are considered. As doping levels increase, the second component becomes more important on the expense of the four-fold oxidized V atoms.

We have shown that, in principal, the transition temperature can be increased by Si doping. Furthermore, the decrease in intensity near the Fermi level with doping, could potentially translate in higher emissivity values, thus in better heat dissipation to the surroundings above the transition temperature. Therefore, further studies on the optical properties of Si doped VO_2 thin films and their potential in solar absorber coatings could be of interest.

Acknowledgements

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