THERMOCHROMIC FILMS OF VO_2:W FOR “SMART” SOLAR ENERGY APPLICATIONS

A. Paone[1], M. Joly[1], R. Sanjines[2], A. Romanyuk[3], J.-L. Scartezzini[1], A. Schüler[1]

[1]*Solar Energy and Building Physics Laboratory (LESO-PB), Swiss Federal Institute of Technology EPFL, CH-1015 Lausanne, Switzerland*

[2]*Institute of Physics of Complex Matter, EPFL, CH-1015 Lausanne, Switzerland*

[3]*Department of Physics, University of Basel, 4056 Basel, Switzerland*

ABSTRACT

Overheating is a problem with the use of active/passive solar energy in thermal solar energy systems. A solution to these problems might be provided by a thermochromic material such as vanadium dioxide. In order to simulate the optical behaviour of multilayered coatings, knowledge on its optical properties is necessary. We determined point-by-point the dielectric function for VO_2:W by ellipsometry. For validation, the solar spectra were measured by spectrophotometry. Such data have been compared with the computer simulations based on the determined optical properties. Finally, we collect optical data by infrared-imaging to detect the switch in emissivity of VO_2:W at around 45°C.

INTRODUCTION

Thermal solar collectors are more and more widespread as a source of renewable energy for domestic hot water production and space heating. The durability of the solar collector materials is however a critical point. Over-heating and the resulting stagnation temperature of the collector are a common problem. During stagnation, high temperatures lead to water evaporation, glycol degradation and stresses in the collector due to the increasing pressure. The elevated temperature leads to degradation of the materials that compose seals, insulation materials and also the selective coating. A solution to this problem could be a coating with optical properties changing at a precise transition temperature. Inorganic materials are able to resist at high temperature preserving a long durability. An organic thermochromic paint exposed to an intense solar irradiation is likely to be much less durable than an inorganic material.

Vanadium dioxide VO_2 undergoes a reversible crystal-structural phase transition from monoclinic to tetragonal (rutile type) accompanied by a strong variation in conductivity, specific heat, optical and magnetic properties.

Vanadium dioxide has already been proposed as a thermochromic coating for windows with variable solar gains adapting to the ambient temperature. At lower temperatures this material behaves as a semiconductor allowing some transmission of solar radiation. Above a critical transition temperature the behaviour switches to metallic, implying an increase in reflectance and a decrease in solar transmission. By doping the material with elements such as tungsten [1], it is possible to lower the transition temperature making it suitable as a thermochromic coating for windows. By doping it e.g. with aluminium [1], it is possible to increase the transition temperature, suggesting its use in solar thermal collectors.

Further applications can be envisaged in the fields of sensing, storage and even logic devices, for example accordable IR mirrors for LASER applications [2, 3, 4, 5], optical storage media [6], uncooled microbolometers [7, 8], modulators and polarisers of submillimitre wave radiation [9].

Thermal evaporation is a simple vacuum deposition method with a high deposition rate resulting in a relatively fast amortization of industrial production equipment. To our knowledge, it has never been applied for preparing VO_2 based films. Reports exist on VO_2 deposition by sputtering, CVD, laser ablation deposition, electron beam deposition, etc. These deposition methods are more expensive, technologically complicated and time consuming than thermal evaporation.

In this study we aim to determine of the most prominent parameters allowing to obtain good switching films, and to characterize the thermochromism of VO_2:W by temperature-dependent electrical and optical measurements.

EXPERIMENTAL SECTION

Thin films of VO_x:W were deposited by thermal evaporation (PVD): the material is melted in an electric resistance crucible so that its pressure is increased to a suitable deposition value. In the high vacuum chamber for thin films deposition, samples up to a size of approx. 20 x 20 cm^2 can be deposited with high homogeneity. As shown in figure 1 (a), samples obtained by our deposition machine are good and homogeneously black selective.

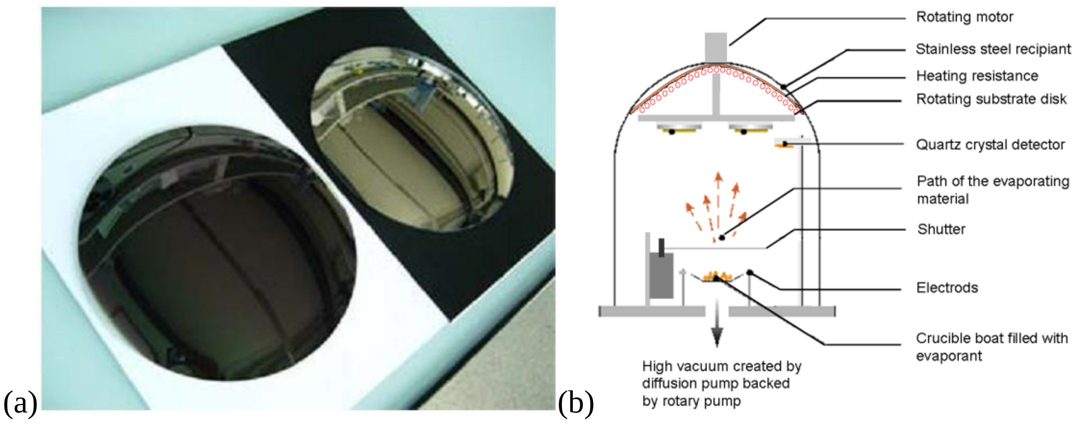

Figure 1: (a): Black absorbing VO_x (left) and mirrorlike film samples (right). (b): a schematic representation of the thermal evaporator used for our experiences.

The deposition of vanadium dioxide was obtained evaporating vanadium in a very well controlled oxygen atmosphere.

In order to obtain a good crystallization of VO_2, substrates were heated up to 550°C during the depositions. A substrate heater was especially installed in the vacuum chamber for this purpose.

In most cases, slides of iron-free white glass were used as substrates.

For measurements of ellipsometry and XPS, thin films were deposited on a silicon wafer (500 µm thick, front side polished, back side etched).

Spectrophotometry in the visible and near infrared wavelength range up to 2500 nm was carried out in order to determine the optical performance of the prepared VO_2:W films. In the visible range the optical properties were investigated using a spectrograph: Oriel MultiSpec 125^{TM} 1/8m and the Oriel detector Instaspec II^{TM}. The Optronic Laboratories Monochromator OL 750-M-S and the associated photosensible detector OL 730 PbS were used for measurements in the near infrared wavelength range. The optical system is equipped with an integrating sphere. In this way, it is possible to measure the total hemispherical transmittance/reflectance (*total* = *diffuse* + *specular*). The optical apparatus can measure even only the diffuse part.

The thermal emissivity of surfaces was inferred from the reflectance measurement of IR variation originating from a heated black hemisphere (at 100°C, instrument: Inglas TIR100).

The thermographic images were taken by an Inframetrics Imaging Radiometer model 760 IR.

XRD analyses were performed at EPFL in the Physics Department (Rigaku equipment with a CuK_α radiation) in the Bragg-Brentano configuration under the supervision of R. Sanjines.

XPS analysis was performed at the University of Basel in the Physics Department under the supervision of A. Romanyuk. The photoelectron spectra were recorded *ex situ* using a VG ESCALAB 210 system.

Ellipsometry is a highly accurate method for investigating the optical properties of thin films. To our knowledge, only little information is available about ellipsometrically determined VO_2:W n and k. Tazawa [10] determined these optical constants from experimental reflectance and transmittance spectra. Ellipsometric measurements were performed at the University of Basel with the Ellipsometer Sentech Instruments GmbH SE850. For high accuracy and reliability, at four different angles of reflection were used for the measurements of the ellipsometric quantities ψ and Δ.

The computer simulations of the spectral reflectance are based on the method of the characteristic matrices [11].

RESULTS AND DISCUSSION

Evidence for the presence of tungsten in these films was found by XPS analyses. A tungsten resistance crucible was use for evaporating vanadium. In our opinion, the W-doping of the films is due to diffusion of W-atoms from the crucible to the molten vanadium.

Four points resistivity measurements

The temperature-dependent conductivity was investigated by a four probes resistivity measurement from ambient temperature up to 130°C.

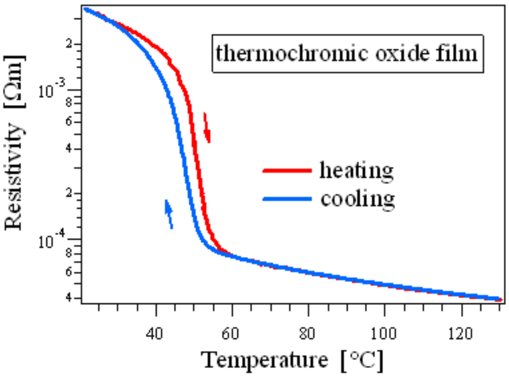

Figure 2: A switching sample which shows a transition temperature around 48 °C.

The resistivity transition results in a high jump of about 2 orders of magnitude.

Optical transmittance and reflectance analyses

To our knowledge, transmittance and reflectance values of spectra VO_2:W thin films are rare in the literature. We measured them in the visible and in the near infrared wavelength range, from 375 nm to 2500 nm.

All of the thin films are deposited on the larger glass substrate: 60 mm x 70 mm x 1 mm.
We measured the substrate temperature with a thermo camera, making sure that the cold state corresponded to the ambient temperature, around 25 °C, and the hot state to around 90 °C.

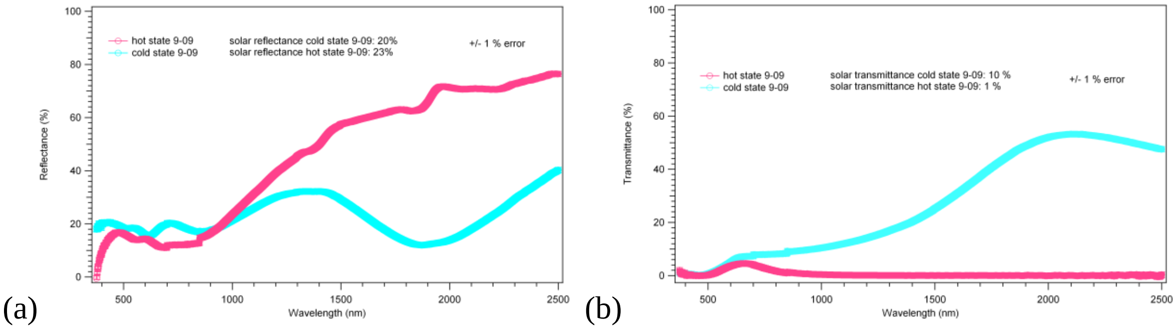

Figure 3: (a): Reflectance of a VO_2:W sample on glass at ambient temperature and at 90°C. (b) Transmittance of a VO_2:W sample on glass at ambient temperature and at 90°C. For each curve the respective fraction of transmitted and reflected energy in the range of the solar spectrum is calculated.

The reflectance between the semiconducting and metallic state changes considerably. Around 2000 nm it switches from 14 % to 71 % [see Fig. 3 (a)].
The transmittance switches from 53 % to around 1 % at the transition around a wavelength of 2100 nm. The optical spectra exhibit systematically a small jump at 880 nm. This can be explained by the use of different detectors for the visible and IR range.
The film's colour clearly changes during the transition from yellowish to brownish making it possible to visually control whether it is in the metallic or in the semiconducting state.
The fraction of the transmitted and reflected energy in the solar range is evaluated by integration of the transmittance and reflectance spectra weighted with the AM 1.5 solar spectrum.

Reflectance analyses by Inglas TIR100 and Inframetrics Imaging Radiometer

Through Inglas TIR100 measurements, the emissivity of a VO_2:W film on a glass substrate was evaluated at 85 %. The same value was found for an uncoated glass. Therefore, in the semiconducting state of VO_2:W, the substrate plays a prevalent role in determining the emissivity behaviour of the entire system (substrate + film).
Due to the measurement principle (infrared reflectivity of a sample at ambient temperature), the emissiometer is not suitable for measuring the emissivity of a heated sample.

For the estimation of the emissivity of our samples in the hot (metallic) state we used a thermographic camera. Our thermographic camera is able to detect radiation in the infrared range of the electromagnetic spectrum (roughly 3 µm - 12 µm).

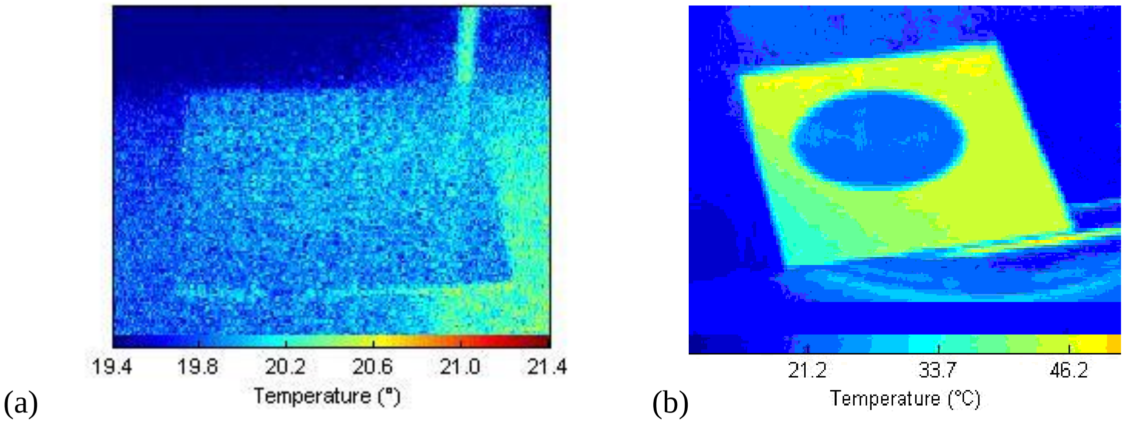

Figure 4: (a): At ambient temperature, VO_2:W is in the semiconducting state transparent for IR radiation. Therefore, the coating is not visible in the thermographic images. (b): In the metallic (hot) state, the film is clearly visible in the thermographic images. The entire system (substrate + film) emissivity is estimated to change from 85 % to 34 %. The saturation of the signal was avoided in all images.

The thermal emissivity of a typical VO_2:W film on glass is estimated at 85% in the cold semiconducting state, and at 34% in the hot metallic state. This corresponds to an emissivity change by a factor of 2.5.

Ellipsometry analyses

These ellipsometric measurements were performed to determine the optical constants in the visible and near infrared range with great accuracy.

The following procedure allows us to determine *n* and *k* of VO_2:W in the semiconducting and metallic state: fitting point by point the measured curves and every time changing the assumed film thickness. We looked for a thickness value which would minimize the root mean square error (RMSE). The initial thickness test value was found by the quartz crystal frequency shift during deposition. A fine adjustment of this value was obtained fitting the measurement with a polynomial formula and looking for the thickness which best minimized the fitting error.

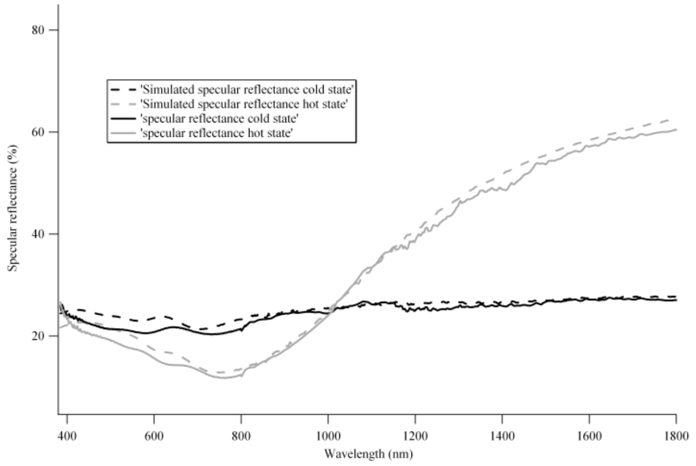

Figure 5: A comparison between a computer simulation and our specular reflectance measured in the semiconducting and metallic states.

We used the optical constants found in this way to simulate the optical behaviour of a VO_2:W layer on a silicon wafer. For a comparison of the simulated reflectance spectra with experimental data see Fig. 5. Only the specular reflectance from the coated front side was taken into account by the simulation. This corresponds to the measurement of specular reflectance from a silicon wafer with an etched back side. The maximum difference between simulation and measurement occurs in the visible spectral range and amounts to 2.5%.

CONCLUSION

Thermal evaporation by resistance heating has been used for depositing VO_2:W films on glass slides and silicon wafer. This deposition technique has the potential for high deposition rates which can be achieved with less complex equipment than that necessary for e.g. reactive magnetron sputtering or electron beam evaporation. To our knowledge, it has never been applied for preparing VO_2 based films.

By W-doping, the transition temperature can be lowered to approximately 45°C.

Our spectrophotometric measurements indicate a maximal transmittance switch for VO_2:W films on glass from 53 % in the semiconducting state to around 1 % in the metallic state at a wavelength of 2100 nm. The maximal reflectance switches in a complementary way, from 14 % to 71 % at a wavelength around 2000 nm.

Between the two states, the emissivity of VO_2:W on glass jumps from 85 % to 34 %.

We investigated the optical constants n and k by ellipsometry in the visible and near infrared. The reproducibility and the accuracy of the ellipsometric measurements have been verified.

The optical simulation based on the determined n and k values yields results which are rather close to the spectrophotometric data.

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