Solar Energy Materials and Solar Cells 183 (2018) 25–33

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

VO_2-based thermally active low emissivity coatings

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ARTICLE INFO

Keywords:
Thermochromism
Low-e coatings
Smart windows
VO_2
Silver
Luminous transmittance

ABSTRACT

Vanadium dioxide is one of the likeliest candidates for future smart window applications due to its self-regulating nature and potentially simple implementation. However, the material is plagued with multiple drawbacks which need to be addressed before its commercialization. Amongst these, its low luminous transmittance has been the subject of many studies. In the present work, we propose to integrate a VO_2 film into a traditional silver-containing low emissivity coating architecture. We first model and discuss the theoretical performance of such a coating in comparison with more standard configurations and demonstrate that the addition of silver offers many advantages for thin VO_2 coatings; mainly an increase of luminous transmittance due to the presence of antireflective coatings while maintaining a high solar transmittance variation vs. temperature. The latter is shown to be the result of a displacement of the maximum transmission variation to lower wavelengths where the solar intensity is higher. We then fabricate prototype samples which confirm the predicted performance. Indeed, a silver-containing sample based on the following architecture Si_3N_4 [57 nm] | VO_2 [27 nm] | Ag [11 nm] | Si_3N_4 [66 nm] is shown to possess the unique combination of a high luminous transmittance of 58.2% in its low temperature state, a solar transmittance variation of 7.1% with the added benefit of a low emissivity of 10%.

1. Introduction

Following the Paris agreement, it has been established that the world must aim at reducing and limiting the Earth's temperature increase to well below 2 °C above pre-industrialized levels [1]. While part of the solution may rely on changing our everyday habits, it has also become obvious that technology has the potential of significantly impacting the energy landscape. In fact, technology can be applied to reduce energy consumption, but can also positively impact our living standards by increasing comfort and the level of control over our surrounding environment [2]. Smart windows, which allow such a control over the solar spectrum input into a building, are one such technology.

Multiple technologies are presently being investigated in this respect such as: liquid crystal-based devices [3], micro-blinds [4], electrochromic [5], thermochromic [6] and gasochromic [7] materials, tunable near-infrared transparent conductive oxides [8], and more. Amongst these proposed solutions, one of the simplest to implement is most probably thermochromic VO_2-based coatings which are self-regulating and require no additional source of energy. Specifically, bulk VO_2 displays semi-conducting properties when below a transition temperature T_c of 68 °C and a metallic-like behaviour when heated to above this same temperature. Correspondingly, and most importantly in the present context, the material goes from a near-infrared (NIR) transparent state to a NIR absorbing/reflecting state. On the other hand, the material possesses many drawbacks which have hindered its implementation into commercial applications; these include: an unappealing yellowish tint, a deposition temperature above 450 °C, a high transition temperature, a low environmental stability and, a low luminous transmittance T_{lum} when a non-negligible solar transmittance variation ΔT_{sol} is desired [9] (see Section 2 for the definitions of T_{lum} and ΔT_{sol}). Table 1 enumerates these main issues in a smart window context as well as some of the solutions which have been proposed and explored.

In the present work, we focus our attention on increasing the luminous transmittance and overall performance of VO_2 films. While the potential gains may not be as impressive and as high as some of the examples shown in Table 1, the proposed solution is much simpler to implement and, to our knowledge, has yet to be exploited. Indeed, we demonstrate, that by incorporating thin VO_2 films (< 80 nm) into a silver-based low-emissivity-type coating architecture (dielectric | metal | dielectric - DMD) we can minimize absorption and reduce reflection losses through antireflective (AR) layers while maintaining a respectable ΔT_{sol}. Although very few authors have explored such a combination, perhaps the closest suggestion to the present work was proposed by Zhang et al. which explored a Ag|VO_2 combination. While they discuss performance enhancements through modeling [24], no clear quantification of the impact on the T_{lum} and the ΔT_{sol} was made and, from a technological point of view, depositing VO_2 on top of Ag

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https://doi.org/10.1016/j.solmat.2018.03.048
Received 6 February 2018; Accepted 28 March 2018

Table 1
Issues with the implementation of intrinsic VO_2 thin films in the context of smart windows and some of their proposed solutions.

Issues	Solutions	References
Yellowish tint	Doping with Au has been shown to result in green-blue films.	[10,11]
High deposition temperature ($>$ 450 °C)	Vanadium films have been deposited at room temperature and then post-annealed in an oxidizing environment.	[12]
	Similarly, vanadium films were post-annealed at 600–650 °C in an oxidizing SO_2 environment.	[13]
	HiPIMS has been shown to allow the deposition of VO_2 films at temperatures as low as 300 °C and even lower.	[6,14]
	Similarly, films have been deposited at 200 °C by applying substrate biasing, but resulting in a slightly lower $\Delta T_{2500\,nm}$ of 50%.	[15]
High transition temperature of 68 °C	Doping with various metals can help reduce the T_c temperature; e.g.: the T_c drops by 23 °C/at% of W.	[16]
	Note that W doping has also been shown to procure the films with a bluish tint (e.g. at 3.5 at%).	[17]
Low environmental stability	The addition of a barrier coating such as Al_2O_3, can increase the lifetime of VO_2 films.	[18]
	HiPIMS films have been shown to be more durable than traditional radiofrequency-sputtered films.	[19]
Low luminous transmittance	Doping with Mg has been shown to increase T_{lum} (e.g.: 10% increase with 7 at% of Mg).	[20]
	Simulations have indicated that a VO_2-covered moth eye structure could possess a T_{lum} of 72.5% in the cold state and a ΔT_{sol} of 15.5%.	[21]
	Modeling of VO_2 nanoparticles embedded in a SiO_2 matrix could potentially possess a T_{lum} of 72% in the low temperature state and a ΔT_{sol} of 20%.	[22,23]

would pose quite a challenge. Another example by Saint-Gobain emphasizes the possibility of an adjustable solar transmittance as well as of applying a current on the silver film (or ITO) to control the VO_2 film's temperature; however, the silver-containing examples all display T_{lum} values below 35% [25].

Silver being such an interesting material, other authors have also discussed its combination with VO_2 in various applications such as active metamaterials [26], nonlinear optical switches with silver or gold covered VO_2 nanoparticles [27], subwavelength hole arrays with variable transmittance [28], silver nanoparticles deposited onto VO_2 with variable surface plasmon resonance or to tune the color and spectral properties of VO_2 [29,30], temperature self-regulating core-shell nanoparticles [31] and tunable thermal emissivity [32].

The film architecture proposed here also benefits from low emissivity (low-e) properties. In fact, a low thermal emissivity and thus high IR reflectance is critical to ensure that the solar energy absorbed by the VO_2 coating, which is then re-emitted through black body radiation in part towards the interior of the building, is rejected. The concept of combining thermochromism and low-e properties is not new and, for example, Kang et al. [33] proposed the addition of a top platinum film; the result was indeed a coating system with a lower emissivity (lowest obtained value of 56% in the low temperature state). Interestingly, they also added a top SiO_2 antireflective coating to enhance T_{lum}, which nevertheless remained quite low ($T_{550\,nm}$ = 37.9%). In a similar effort, silver nanowires have also been added to the surface of VO_2 to lower its emissivity (lowest value of 60.3%) [34]. An obvious alternative to metal films are transparent conductive oxides (TCO) and multiple examples of their implementation can be found in the literature. For example, VO_2 films where grown over $F{:}SnO_2$ films with results which are in line with the present study (13% emissivity) [35]. These polycrystalline TCO films were also shown to be beneficial for VO_2 growth by enhancing crystallinity and lowering the deposition temperature.

Thus, in this work, we first model the impact of the addition of silver in combination with VO_2 by comparing the thermochromic performance of three model stacks, namely, a single VO_2 film, an antireflection-based $Si_3N_4|VO_2|Si_3N_4$ stack, and finally our proposed thermally active low-e $Si_3N_4|VO_2|Ag|Si_3N_4$ architecture. We then demonstrate that with silver, the ΔT_{sol} can be maintained at higher levels for VO_2 thicknesses below 80 nm. Follows an analysis of fabricated prototype samples which confirm our initial modeling results and which demonstrate a truly unique combination of performance indices for a thin VO_2-based device ($<$ 30 nm) resulting in a high luminous transmittance, a respectable solar variation, and a low emissivity.

2. Experimental methodology

2.1. Optical modeling

The theoretical optical performance of the studied architectures was performed by the implementation of the matrix formalism in *Matlab* [36]. Note that the backside reflection of the glass substrate was included during modeling. The results were additionally validated with *OpenFilters* [37]; the later was also used when modeling specific optimized architectures obtained using the *Matlab* program. The calculations where performed using the list of materials shown in Table 2. The silver properties [38] were extrapolated from 1938 nm to 2500 nm by using a Drude model implemented in the *CompleteEase* software from J.A. Woollam Co. Three specific architectures were studied:

- Standard: B270 | VO_2
- Antireflective: B270 | Si_3N_4 | VO_2 | Si_3N_4
- Low-e-based: B270 | Si_3N_4 | VO_2 |Ag | Si_3N_4

Si_3N_4 films were chosen as the antireflective dielectric material for practical reasons as from a process point of view, it is simpler to sputter a nitride over silver without the use of a protective film; indeed, in the specific case of oxides a thin metal layer is typically added [40]. In addition, it is also a good diffusion barrier, which turns out to be critical when depositing VO_2 onto glass at high temperatures [6]. The performance of the different architectures was assessed through the luminous transmittance T_{lum} (at low temperature) and the solar transmission variation between the low and high temperature states, ΔT_{sol}. Both these parameters were calculated using the following equations integrated at every 1 nm:

Table 2
Thickness range and optical properties of the materials used during modeling.

Material	Thickness range [nm]	*n* @ 550 nm	*k* @ 550 nm	Source
B270 substrate	2 mm	1.524	$< 10^{-4}$	Measured
Si_3N_4	0 − 200	2.037	6.9×10^{-5}	[39]
VO_2 [@ 21 °C]	0 − 120	2.932	0.534	[14]
VO_2 [@ 90 °C]	0 − 120	2.465	0.561	[14]
Ag	8	0.060	3.598	[38]