Temperature-agile and Structure-tunable Optical Properties of VO_2/Ag Thin Films

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Abstract

By integrating together the VO_2's unique near room-temperature (RT) semiconductor-metal (S-M) phase transition with a thin layer silver's (Ag) plasmonic properties, VO_2/Ag multilayers could present a much enhanced optical transmission change when increasing the temperature from RT to over VO_2's S-M phase transition temperature. Changing VO_2 and Ag layer thicknesses can also significantly tune their transmission and absorption properties, which could lead to a few useful designs in optoelectronic and energy-saving industries.

1. Introduction

A multilayer with its optical properties to be actively modulated via external physical parameters can find many potential applications in a few emerging technology areas including optoelectronics as either components or sub-systems. In certain security-related cases a smart window for those sensors monitoring various external physical parameters requires an instant response to an unexpected incident radiation. For example when incident with a thermal radiation in a harsh environment, the window should instantly become highly reflective, realizing a unique sensor protection function. Similarly, this function can also be applied to building windows for energy-saving. A thermochromic window highly reflective to thermal radiation and automatically switchable by the temperature can effectively prevent a building from overheating by solar irradiation in summer time. In these regards, a temperature-agile and structurally tunable multilayer coating combining the use of temperature-active materials is highly desirable, and the coating should be simple in structure, cost effective in material usage, easy in film fabrication, and flexibility to be coated on substrate materials such as regular glasses.

Vanadium dioxide (VO_2) thin films have been the subject of intensive research in recent years. It has a reversible first-order semiconductor-metal (S-M) phase transition under a few different external excitations. When changing the temperature, for example, it has a phase transition at around 68℃. During the S-M phase transition, VO_2 experiences dramatic changes in many properties incldluing dielectric constant and electrical conductivity [1, 2]. Very encouragingly, via doping this phase transition temperature can be almost linearly lowered to ~40 ℃[3], and its closeness to RT makes the material more attractive to the above-discussed security photonics and energy-saving windows applications. In the past, there are a few researches reported the use of VO_2-embedded noble metal/VO_2 films to improve their optical performance [4-6]. In those designs, thin layer noble metal such as platinum was usually used as the surface layer with a goal to modify the refection to the infrared. This layer of noble metal has to be very thin in order not to sacrifice the optical transmission to the visible light, and this causes technical problems related to the film growth and then adds limitation to material selection on the noble metal only. In this research via simulations we have used a simple structure of VO_2 and plasmonic metallic silver (embedded beneath the VO_2 layer) to be potentially made on glass substrates, and investigated their optical transmission and absorption over a wide temperature range crossing through the VO_2 phase transition temperature and over a range of structural changes. It was experimentally demonstrated before that by adding a thin layer of Ag beneath to a semiconductor layer the optical transmission can be significantly modified [7], due to the plasmonic behavior and the thickness change of the Ag layer. Here embedding a thin Ag layer could therefore utilize both benefits from the temperature agility of VO_2 and from the plasmonic enhancement of the embedded Ag thin layer. An additional benefit is that the structure could tolerate relatively thicker metallic layer which may ease the thin film deposition.

2. Computational method

The schematic structure includes a thin Ag layer sandwiched between a VO_2 layer and a K9 glass substrate. In our simulations, we mapped the VO_2 thickness from very thin to about 200 nm, and changed the Ag thickness from 0 (no Ag layer) to 15 nm at an interval of 5 nm. A wavelength range from 0.35 to 2 μm, from ultraviolet (UV) to the mid-infrared (IR) covering the major solar spectrum, was also swept through in the investigation. Dielectric constants (*n* and *k*) of VO_2 used in our simulations was taken from interpolating of the reported experimental spectroscopic data [8-9], and were shown in Fig.1a and Fig.1b, respectively. To be brief and simple, only a few lines corresponding to a few temperatures aside the phase transition temperature were shown. Normally the material is relatively transparent in its semiconductor state, and reflective and absorptive in the metal state, in the near-infrared spectrum. Dielectric constant of silver is taken from the tabulated data in [10]. In the interested wavelength range, the K9 glass's dispersion is small comparing to those of silver and VO_2, and was then neglected. We used a constant K9's refractive index of 1.51. The simulations were executed following the transfer matrix method [11].The method generates analytic results from the Maxwell's equations in horizontally infinite multilayer structures in our cases here, which are equivalent to the Fresnel's formulation but much more convenient [12].

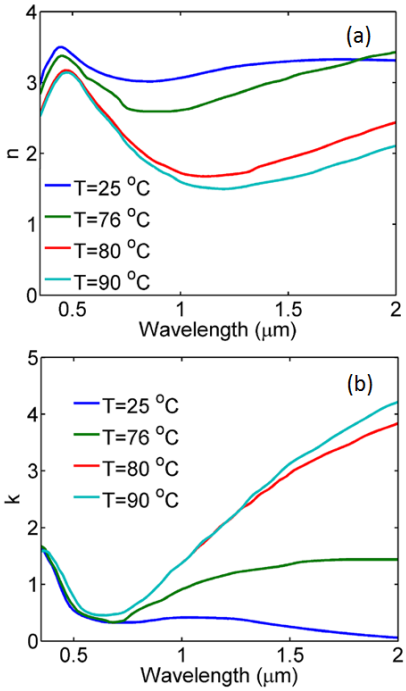

Fig.1 (a) and (b) are real and imaginary refractive indices of VO_2 in the visible to near-IR spectrum range at a few different temperatures.

3. Results and discussion

3.1. Adding a ultra-thin silver layer

We first investigated the case of embedding a thin Ag layer to the structure with a fixed VO_2 thickness of 50 nm, comparing to the case of no Ag layer. Fig. 2a and 2b show both transmission and absorption spectra for the structure with different Ag thicknesses of 0, 5, 10 to 15 nm, respectively, with the VO_2 in its semiconductor (solid lines marked with 's', selected at 25 °C) and metallic phases (dotted lines as 'm', selected at 80 °C). In Fig. 2a, optical transmission for the metallic VO_2 state always reduces as the Ag thickness increases. Whereas in the dielectric state, change of the optical transmission can be roughly divided into three wavelength sections: < 0.6, 0.6-1.2, and > 1.2 μm. When below 0.6 μm, the transmission presents a monotonous reduction as the Ag thickness increasing. When above 0.6 μm, adding a thin Ag layer first enhances the transmission, and then reduces it. In the range of 0.6-1.2 μm, however, this enhancement extends to the case with an Ag thickness of 10 nm, from that of 5nm when the wavelength is > 1.2 μm.

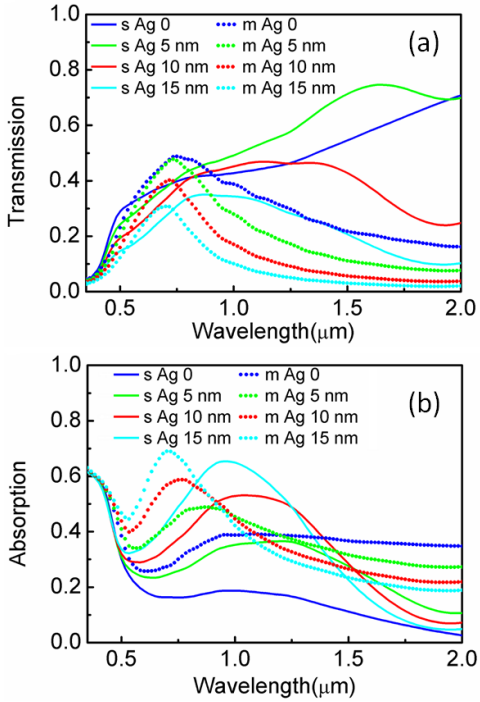

Fig. 2 Transmission and absorption in cases with and without the thin Ag layer, with 's' stands for the semiconductor VO_2, and 'm' for metallic. The VO_2 layer thickness is fixed at 50nm.

In general, optical transmission of a multilayer may reflect the variations in absorption of the materials and the reflection by multiple interfaces. Fig. 2b shows the optical absorption in dielectric (semiconductor) and metallic VO_2 states when increasing the Ag thickness, monitored by simulating the exact electrical field inside the multilayer. In the metallic state, the multilayer is all metallic and it shows three distinct absorptions: sharp increasing in absorption from photoionization inside the skin layer under high energy UV photon irradiations, plasmon absorption as the peak at ~0.6 μm, and absorption from free carriers excited by the near IR photons (> 1 μm). The monotonous reduction in transmission as the Ag thickness increasing in the metallic VO_2 shown in Fig 2a can be explained by the superposition of all three absorption mechanisms discussed above.

When VO_2 is in the dielectric state, however, as usual it presents photoionization absorption for high energy UV photons and then multiple interface reflections for visible and IR photons at the case of no Ag layer. Adding a thin layer of Ag to the structure excites the plasmon absorption in the wavelength range around 1 μm. This plasmon absorption is enhancing and then blue-shifts as the Ag thickness increases. This corresponds well to the observation in Ag nanoparticles [13]. In the long wavelength range, adding the Ag layer raises the free carrier absorption from the near IR photon excitation. Additionally, a planar cavity resonance inside the dielectric VO_2 layer has to be considered here for those photons having wavelengths shorter than an effective quarter wavelength of the cavity ($\lambda/4n$, for a 50 nm thick VO_2 this is around 0.6 μm). This resonance will overlap and modulate the reflection when the spectrum having wavelengths smaller than $\lambda/4n \sim 0.6$ μm, and when the Ag thickness changes.

3.2. Structure-tunable optical transmission and absorption

For a particular application, a useful parameter to be derived from Fig. 2a is the optical transmission difference between the VO_2's dielectric and metallic states. For potential photonic applications involving lasers, for example, wavelengths of 1.064 μm (Nd^{3+}:YAG) and 1.55 μm (Er^{3+}:Fiber) would be of the major interests. For solar energy applications, for another example, we may be interested in the 'hot' IR wavelength range. According to above Fig. 2a results and considering the Ag thin film's fabrication/quality issue, in our subsequent simulations we will choose the Ag's thickness of 10 nm, which is not too thin but still maintains acceptable bi-status transmission contrasts over a fairly large IR wavelength range. We were then mapping both transmission and absorption over a wavelength range from 0.35 to 2 μm and over a VO_2 thickness from very thin to 0.2 μm (in the semiconductor state), at both cases of without and with Ag (10 nm thick). Fig.3 (a-d) shows the optical transmission (a and c) and absorption (b and d) mapping spectra for the bare VO_2 film (a and b) and the structure with Ag layer (c and d), with the varying VO_2 thickness and the wavelength.

Apparently, an enhanced optical transmission occurs as a dark strip in Fig. 3c in the case of adding the Ag layer, and the enhancement shifts to longer wavelength as the VO_2 thickness increases. This is a mainly from the cavity resonance response inside the VO_2 layer that is affected by plasmon and free carrier absorptions inside the metallic layer and also possibly inside the semiconductor layers (the changing amplitude along the dark strip). Possible plasmon and free carrier contribution to the absorption inside the semiconductor layer can be clearly seen in Fig. 3d. They are very weak in the case of the bare VO_2 structure, as only a few light color contours can be seen in the similar area in a Fig. 3b to that in Fig. 3d. Fig. 3 gives the necessary instruction to further device designing, and indicates the structure's better performance for long wavelengths where the plasmon-related absorption is reducing (beyond the 2 μm wavelength range).

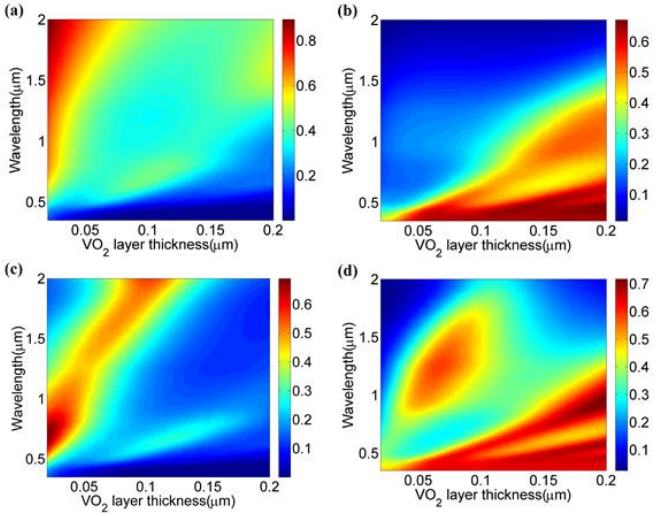

Fig. 3 Mapping transmission and absorption with varying VO_2 thickness and incident wavelength. (a) and (b) are for bare VO_2, respectively. (c) and (d) are for the case with a 10 nm Ag layer.

3.3. Temperature-agile transmission and absorption

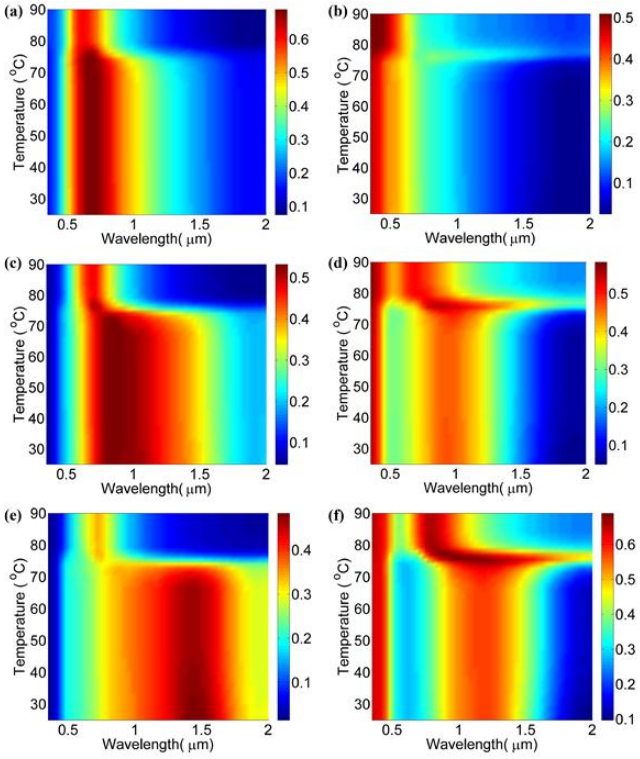

Fig. 4 Mappings transmission (a, c, e) and absorption (b, d, f) spectra with varying temperature and VO_2 layer thicknesses ((a, b) for 20 nm, (c, d) for 40 nm, (e, f) for 60 nm). The Ag layer was fixed at 10 nm.

Figure 4 shows the optical transmission and absorption spectra with varying temperature and VO_2 layer thickness, when the silver layer was fixed at 10 nm. We neglected a possible reduction of the VO_2's S-M phase transition temperature caused by overlapping the VO_2 with Ag, and

fixed the phase transition temperature at ~70 ^{o}C in all the following simulations. A noticeable phenomenon is the abrupt change (from high to low) in optical transmission when the VO_2 layer changes its state from semiconductor to metallic. This change occurs mainly in the visible to near infrared wavelength range, which shifts and expands in range when increasing the VO_2 thickness from 20 to 60 nm. This range is roughly in 0.5-1.0 μm at the VO_2 thickness of 20 nm, shifts and expands to 0.6 to 1.5 μm at 40 nm, and further to 0.75 to 1.75 μm at 60 nm. This change can be explained by overlapping the plasmon absorption, free carrier absorption, and resonance cavity effect discussed above, and can be also clearly seen in Fig. 4b, 4d, and 4f. When below 0.4 μm, that little optical transmission change when crossing the phase transition temperature is because of the high absorption of both VO_2 states over those short UV photons. Such results in Fig. 4 are attractive to future energy-saving and specific photonic applications.

4. Conclusions

An integration of near RT phase-transition material VO_2 with plasmonic metallic silver as temperature-agile and structure-tunable coatings on glasses was proposed and fully investigated by simulations. Adding a thin Ag layer enhances the optical transmission when VO_2 is in its dielectric state. The optical performance can be further tuned by changing the layer thicknesses. Such properties can be explained by photoionization by UV, plasmon absorption, free-carrier absorption, and resonant cavity effect.

Acknowledgements

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