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Light modulation in phase change disordered metamaterial - A smart cermet concept

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A B S T R A C T

Cermet coatings are popular solar selective absorbers as they allow capturing most of the solar energy while minimising radiative losses. Embedded metallic nanoparticles in dielectric matrices promote multiple internal reflection of light and provide an overall low emissivity. VO_2 in the metamaterial state is regarded in this study as a responsive mixed phase comprising metallic rutile VO_2 inclusions in semiconducting monoclinic VO_2 phase mimicking cermet. The smart cermet responds to thermal stimuli by modulating the size of the metallic inclusions and thereby enabling the manipulation of their interaction with light. The highly reliable and reproducible response of the smart cermet corroborates with the observed ramp reversal memory effect in VO_2. We demonstrate a thermally controlled 85% emissivity switch taking advantage of the narrow hysteresis and tuning abilities of the disordered metamaterial.

Introduction

Cermets are metal-dielectric composites in which metal particles are embedded in dielectric matrices as displayed in Fig. 1. Cermet coatings are used as effective spectrally-selective absorbers due to their high solar absorbance and low thermal emittance [1,2]. The properties of the cermet strongly depend on the volume fraction of the metal inclusions in addition to their chemical nature, size, shape and dispersion within the matrix [3]. Nevertheless, the properties of the cermet coatings are frozen upon synthesis as the parameters influencing the optical properties can no longer be altered. Therefore, the development of traditional cermet materials for light modulation sounds compromised.

One of the most popular and well-studied mechanisms for light modulation relies on materials with engineered structures to influence the nature of light. These materials are known as metamaterials and the phenomenon of light modulation through engineered surface modifications is termed as optical topological transition [4,5]. Perfect solar absorbers based on metamaterials were demonstrated by fabricating specific shapes and configurations of metallic structures on dielectric matrix. By varying the size and configuration, the spectral window of the perfect absorption can be adjusted [6,7].

Relevant research was reported on emissivity control devices for their implementation in space applications. Programmable emissivity switching is crucial for spacecraft and satellite surfaces, but their implementation often includes tedious fabrication process comprising bulky and energy inefficient mechanisms [8–11]. Significant research has been done in the field of thermal management for spacecraft and satellites, due to varying exposure to sun illumination. Variable heat rejection surfaces are used to control the heat dissipation mechanisms. One of the earliest techniques of thermal management of spacecraft is by the use of mechanical or electric louvers, where actuating the louvers exposes or conceals a section of surface with a contrasting emissivity, thereby reflecting the IR radiation on demand. Electric louvers based on micro-electro-mechanical systems (MEMS) were introduced to further improve the same mechanism and miniaturise the package [9]. Here micro-sized windows open and close on demand to reject IR radiation. An advantage of MEMS based louvers over their bulk mechanical counterparts is the possibility to achieve partial IR rejection by actuating only a part of the micro-louvers [9]. Electrochromic devices that rely on chemical changes to vary the

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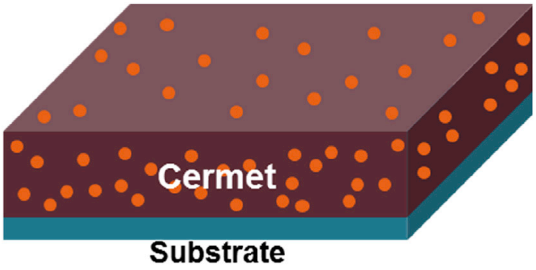

Fig. 1. Schematic presentation of cermet coating.

emissivity of the surface are investigated as alternative solutions to change the optical properties of the radiating surface. An electrically triggered redox reaction on conductive polymers leads to a change of emissivity (ΔƐ). The absence of moving parts is advantageous in terms of production cost, reliability and integration [10]. Nevertheless, slow switching; high input power and the relatively low ΔƐ remain clear drawbacks. This strengthens the need of developing variable emissivity coatings that offer large amplitude of emissivity change, with negligible switching delay and low actuation power. The coatings should also virtually have no loss in performance over a longer time period and should resist environmental degradation. Therefore, inorganic metal oxide coatings with intrinsic phase transition behaviour are an appealing alternative. Ideally the phase transition occurs instantaneously between two strongly contrasting emissivity states without involving any chemical change.

An ideal candidate for such application would be a coating material that switches reliably between distinct values of emissivity, and which is simple to fabricate and integrate, while consuming fraction of the power needed for existing technologies.

Vanadium dioxide is a strongly correlated material featuring a semiconducting-to-metal transition (SMT) near room temperature. In contrast to the metallic phase, the low temperature semiconducting phase features high infrared transmission and high thermal emissivity. The transition occurs with a narrow hysteresis, revealing a temperature range (64–68 °C) where vanadium oxide features the coexistence of the metallic and semiconducting phases. This, so called disordered VO_2 metamaterial is analogous to a cermet. Upon the increase of temperature, metallic inclusions nucleate and grow throughout the semiconducting phase [12]. In this article we introduce the concept of “smart cermet” material with tuneable optical properties based on disordered VO_2 metamaterial. The concept of tunability is addressed by temperature-enabled control of the size and density of metallic particles in the dielectric matrix which in turn vary the emissivity of the coating. The unique feature of VO_2-based smart cermet is that, both dielectric matrix and metallic particles are one and the same material at different phases. Therefore, a single layer of VO_2 can be manipulated to feature (i) a fully dielectric state, (ii) a variable state with metallic inclusions embedded in the dielectric matrix, or (iii) a fully metallic state, by controlling the temperature at which it is operated. Such characteristics are not accessible with conventional cermet coatings. Thermally triggered emissivity modulation is emphasized in this study.

Methods

VO_2 films were deposited on silicon substrates using direct liquid injection MOCVD (MC200 from Annealsys), which is a stagnation point-flow warm-walled reactor. Cyclohexane solution containing 5×10^{-3} mol/l of vanadium (IV) oxy-tri-isopropoxide $[VO(^iOC_3H_7)_3]$ is used as a precursor feedstock that was maintained under nitrogen atmosphere at room temperature before its injection into the evaporation chamber. The precursor delivery was performed at a frequency of 2 Hz and a feeding rate of 1 g/min. The pressure and temperature of the evaporation chamber were maintained at 0.6 mbar and 200 °C during deposition respectively. The substrate is maintained at 600 °C during the 2 h of deposition and the subsequent heat treatments.

One hour annealing was performed right after the deposition under oxygen partial pressure of 1×10^{-2} mbar. The sample is then further subjected to annealing under vacuum acting as a reducing atmosphere for 4 h. The chamber is allowed to cool down to withdraw the sample. All depositions were carried out on 4-inch silicon wafers with an upper native oxide layer. Uniform and high quality VO_2 films were observed throughout the wafers with excellent homogeneity.

Film thickness was measured using an Alpha step d-500 profilometer from KLA-Tencor, whereas the Infrared image analysis was conducted using the FLIR X6580SC thermal camera operating in the spectral range of 1.5–5.1 μm. A CVD-grown CNT on silicon was used as a reference black body for an accurate determination of temperature, which is necessary to assess the emissivity change of coated VO_2. Precise temperature control was achieved through a Linkam TMS heating stage with programmable heating and cooling profiles. The stage is widely used for its accurate temperature control of heating/cooling rates with high ability to maintain a particular temperature for extended periods (>100 h) and has the ability to increase or decrease the temperature at the rate of up to 150 °C/min with no measurable overshoot. The heating or cooling pulses are programmed, and the set values are produced with divergences less than 0.01 °C. The inspection of the surface morphology was performed by Scanning Electron Microscopy (SEM) at a working distance of 4 mm and an acceleration voltage of 5 kV. It is worth mentioning that the electron beam of the SEM induces the SMT of VO_2 from the semiconducting monoclinic phase to the metallic rutile, which is beneficial for the charge dissipation. The identification of the crystalline phases was performed with X-ray diffraction (XRD: Bruker D8 and with CuKα as the X-ray source) and Raman scattering (InVia, Renishaw with a 532 nm laser).

Results and discussion

The process used for the synthesis of VO_2 includes CVD deposition and an oxidative sintering as a post-deposition heat treatment. Using this process the deposition rate was evaluated at ~10 nm/min. The prepared films are clearly identified as monoclinic VO_2 at room temperature by Raman spectroscopy. Displayed spectrum in Fig. 2a features all characteristic Raman bands of the VO_2 monoclinic phase, which can be clearly distinguished from the other phases of vanadium oxide [13]. The obtained films do not feature any Raman band above 68 °C, which indicates the occurrence of a structural transition.

The room temperature X-ray diffractogram, Fig. 2b, of the obtained films confirms their identification as crystalline monoclinic VO_2. The SEM surface inspection, Fig. 2c, reveals a dense structure with large grains witnessing an efficient sintering of the film.

Thermal camera was implemented in this study to investigate the VO_2 phase transition from semiconducting monoclinic to the metallic rutile that occurs with thermal cycling. As the metallic phase features a low thermal emittance, the surface appears colder above the transition upon heating, a phenomenon that was termed as negative differential thermal emittance [14]. The VO_2 emissivity versus temperature upon cycling between 60 and 70 °C, Fig. 3, features three distinct regions marked (a), (b) and (c). During heating stage the system undergoes an abrupt semiconductor to metal transition (SMT) at 67.5 °C resulting in an emissivity drop