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Nanostructured thin films for solar selective absorbers and infrared selective emitters

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ABSTRACT

Solar technologies require improved material performances or new materials functions, either to improve energy capture or to develop new conversion principles. This work presents a low cost pathway to realize 2D nanophotonic molybdenum crystals having a transition in their optical properties with a tunable cut-off wavelength. These nanostructured materials have a dual function. They can be used as selective solar absorbers and/or selective infrared emitters. This novel pathway for producing low cost nanostructured materials creates new opportunities for solar capture in Concentrated Solar Power, Solar Thermophotovoltaics, Solar Thermo-Electrical Generators and for infrared emission control in thermophotovoltaic technologies.

1. Introduction

Engineering of the optical functions of surfaces and thin films is becoming critical for many applications, especially for renewable energy technologies. There is for example a strong need of selective absorbers made of refractory materials able to absorb almost all the incident solar radiation with a very limited infrared emission for solar thermal and Concentrated Solar Power (CSP) systems. Selective solar absorbers are key elements of all existing solar thermal systems which aim at producing heat and electricity. In these technologies, a surface receives the solar radiation and the material is designed to have the highest optical absorptance of the solar radiation in the visible wavelength range where the solar intensity is the highest. It also has a low emittance in the infrared range in order to avoid radiative losses. This kind of material having different optical properties depending on the wavelength range can be also a good candidate to control the spectrum of infrared emission that can be coupled with thermophotovoltaic (TPV) cells to obtain an efficient thermal to electrical conversion. These infrared emitter materials are used in the domain of thermophotovoltaics and more recently in solar thermophotovoltaics (STPV). An accurate control of the optical function of the infrared emitter material is mandatory for TPV conversion efficiency to emit in the wavelength range where the TPV cell conversion is the highest. Current material solutions for those two functions usually consist in deposited interferential thin films or cermet materials [1,2]. In the fields of solar thermal and CSP, commercial products are only produced so far by interferential of cermet films by Almeco, Nitto Kohki, Turbosun, GRINM, Alanod Solar, Ikarus Coatings, S-Solar, Angelantoni, Siemens, Schott [3]. Their solar absorptance values are in the 90–96% range, most often at least at 95%. In parallel, researchers also proposed structured materials to realize the same type of optical functions. Three dimensional photonic crystals (PhC) realized with expensive microtechnology patterning techniques were proposed [4]. Structured surfaces consisting in 2D photonic crystals were also proposed [5] because they present interesting properties compared to interferential solutions, as for example a higher acceptance angle for absorption. They can also potentially be fabricated with only one material, avoiding by this way the adhesion issues related to the differences of thermal expansion coefficients between substrate and films when used at high temperatures. Even if processes for low cost production are being investigated [6], most realizations still use expensive lithography steps needed for structuring materials at the nanoscale.

This work presents a low cost pathway to realize 2D nanophotonic crystals with optimized selective optical properties and a tunable cut-off wavelength. They are realized with molybdenum, a refractory material able to sustain high temperatures. We show in this work how the fabrication process can be optimized to obtain a dual function as selective solar absorber and/or selective infrared emitter by controlling the cut-off wavelength in the 1–2.5 μm wavelength range.

2. Experimental and methods

2.1. Material deposition and structuration

The fabrication of studied materials was done with a four steps process: cleaning of the substrate, deposition of an adhesion layer,

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deposition of the refractory metal and nanostructuration of the film by reactive ion etching. This approach is comparable to the one we presented earlier [5] but the process flow has been simplified here with the removal of the micromasking sphere deposition step to reduce the fabrication cost. The deposition and etching steps were also studied and optimized to allow an adaptation of the cut-off wavelength of the optical properties. In this study, the substrates were silicon wafers. They were cleaned in acetone ultrasound bath, then rinsed in ethanol and dried with nitrogen. Prior to molybdenum deposition, a thin film of titanium was deposited on the substrates to improve adhesion. The first deposition step was of a 100 nm layer of titanium performed in an Alcatel SCM600 sputtering system at a deposition rate of 25 nm/min with a pressure of 7 mT, an Argon flow rate of 70 sccm and a power of 500 W on a 200 mm cathode. Then the deposition of molybdenum was performed in a Perkin Elmer PE 2400 DC sputtering system at a deposition rate of 65 nm/min, using a pressure of 3 mT, an Argon flow of 30 sccm and a DC power of 700 W for a 200 mm diameter target. The different film thicknesses were realized by varying the deposition times with the same process conditions. Finally, the etching process was performed in a Nextral NE110 RIE system using a SOFIE Instrument interferometric endpoint detection system using a laser emitting at 677.4 nm. The process parameters were 5 sccm of SF6, 3 sccm of O2 at a pressure of 50 mT and a RF power (13.56 GHz) of 10 W on a silicon chuck of 100 mm of diameter (corresponding to a power density of 0.13 W/cm^2). The end of the process was determined by the first minimum on the endpoint detection system, corresponding to a minimum of reflection at the 677.4 nm wavelength in the visible range.

2.2. Material characterization

The morphology of deposited films as well as of nanostructured films were characterized by Scanning Electron Microscopy (SEM) in a LEO 1530 equipment. The optical properties of the films were determined by measuring the reflectance of samples by spectrophotometry in the visible and infrared ranges. A Perkin Elmer Lambda 950 and a Bruker Equinoxe 55 spectrophotometers were used respectively for the visible and IR ranges. A sphere was used to measure the total hemispherical reflectance.

According to the Kirchoff's law, the thermal emittance $\varepsilon(\lambda)$ of a surface is equivalent to the absorptance $\alpha(\lambda)$ and for opaque materials both are related to the total hemispherical reflectance $R(\lambda)$ by the following law:

$$\alpha(\lambda) = \varepsilon(\lambda) = 1 - R(\lambda) \quad (1)$$

The performance of the material as a solar absorber can be estimated by calculating the solar absorptance A according to Eq. (2), where $I_{AM1.5}$ (λ) refers to the incident solar power which can be described by the AM1.5 spectrum. λ_{min} and λ_{max} values are respectively 320 nm and 2.5 μm.

$$A = \frac{\int_{\lambda min}^{\lambda max} (1\text{-}R(\lambda)).IAM1.5(\lambda).d\lambda}{\int_{\lambda min}^{\lambda max} IAM1.5(\lambda).d\lambda} \quad (2)$$

The thermal emittance $\varepsilon(T)$ at the temperature T can be calculated by Eq. (3), where I_{BB} (λ,T) is the radiative power emitted by the blackbody at the wavelength λ and the temperature T and given by the Planck law.

$$\varepsilon(T) = \frac{\int_{\lambda min}^{\lambda max} (1\text{-}R(\lambda)).IBB(\lambda,T).d\lambda}{\int_{\lambda min}^{\lambda max} IBB(\lambda,T).d\lambda} \quad (3)$$

The values of absorptance and emittance can thus be determined thanks to the acquisition of the total reflectance spectra $R(\lambda)$ in the visible and IR ranges, between 320 nm (λ_{min}) and 20 μm (λ_{max}) in this study.

The performance of the material as a selective IR emitter for a TPV cell can be estimated by its capability of cutting the blackbody emission at wavelengths larger than the cut-off wavelength of the TPV cell. Practically, TPV cells have a good photon to electrical conversion efficiency for a limited wavelength range, and the photon energy needs to be higher than their bandgap. The corresponding cut-off wavelength is for example 2.3 μm for InGaAsSb cells and 1.7 μm for GaSb cells. The emitted IR spectra can be established by calculating for each wavelength the product of the thermal emittance $\varepsilon(\lambda)$ and the spectral radiance $I_{BB}(\lambda,T)$ of the blackbody at the temperature T. Eq. (4) shows how can be calculate the figure of merit consisting in the spectral efficiency $\eta(T)$ representing the ratio of useful thermal energy emitted below the bandgap wavelength λ_{TPV} compared to the total thermal energy emitted by the surface. λ_{min} and λ_{max} are respectively 320 nm and 20 μm. λ_{TPV} is equal to 1.7 and 2.3 μm respectively for GaSb and InGaAsSb TPV cells.

$$\eta(T) = \frac{\int_{\lambda min}^{\lambda TPV} (1\text{-}R(\lambda)).IBB(\lambda,T).d\lambda}{\int_{\lambda min}^{\lambda max} (1\text{-}R(\lambda)).IBB(\lambda,T).d\lambda} \quad (4)$$

3. Results and discussion

This part presents the results obtained in terms of surface morphologies and optical characterizations. Then, the performances of the nanostructured surfaces are established and discussed with respect to the two applications: selective solar absorbers and selective thermal emitters.

3.1. Morphology before and after the structuration process

Fig. 1 presents the morphologies of three different molybdenum films deposited with three deposition times: 17 min, 22.5 min, 40 min. Thicknesses are respectively 1130 nm, 1500 nm and 2600 nm. The morphology of the films is clearly columnar. The columns and grains are slightly larger when the thickness of the film increases. The density of the film is slightly lower in the upper part of the thicker films, with some voids between columns. This morphology was optimized because it impacts directly the structure of the films after the etching step of structuration.

The etching process was then performed in a fluorinated plasma producing etchant species that react with molybdenum. During the etching process, the endpoint system acquired the signal of the laser reflected intensity. We found that the minimum of reflectance at the laser wavelength corresponded to a minimum of reflectance in the overall visible range, which is desired for a good solar absorber. This signal was though used to stop the etching process at the time corresponding to the best optical performance in terms of reflectance. Fig. 2 shows examples of endpoint traces obtained for four different thicknesses of deposited molybdenum. The etching process times varies from 550 to 720 s, depending on the initial film thickness and on the etching etch rate.

The resulting morphologies of the surface are illustrated in Fig. 3. The etching process resulted in nanostructured molybdenum films thanks to a preferential attack of the film in the column and grain boundaries. This preferential attack and selectivity of etching between boundaries and columns is dependent on the deposited film as well as the etching process parameters, especially the etching chemistry (ratio of SF6 versus O2 flows) and the directionality of species arriving on the surface (controlled by power and pressure). They were optimized to achieve the best optical properties presented in the next section dedicated to the optical characterization results.

3.2. Optical characterizations

Molybdenum films were characterized after deposition. Fig. 4 shows the reflectance spectra in the visible and IR ranges for four different