Thin cadmium sulphide film for radiative cooling application

M. Benlattar a,b, E.M. Oualim a,*, T. Mouhib a, M. Harmouchi a,
A. Mouhsen a, A. Belafhal b,*

a Laboratoire d’Optique Appliquée et Transfert d’Energie, Faculté des Sciences et Techniques, Université Hassan 1er, B.P. 461 Settat, Morocco
b Laboratoire de Physique Moléculaires, Département de Physique, B.P. 20, Faculté des Sciences, Université Chouaïb Doukkali, 24000 El Jadida, Morocco

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Abstract

The present work reports the possibility of a specific shield (CdS) to provide passive cooling for the purpose of reducing the use of classical active method. The ideal radiation shield would completely block solar radiation, but allow complete transmission in the “atmospheric-window” region.

Chemical solution deposition of the thin film CdS (1 mm) for radiative cooling is described and optical properties of the thin film were measured by an OL-750 Spectroradiometer. The radiative properties of the shield improved optical properties of cooling purposes; which indicates that it has very low IR band reflectance and is transparent across the full 8–13 μm.

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1. Introduction

The phenomenon of radiative cooling uses the fact that the thermal energy emitted by a clear sky in the “window region” (8–13 μm) is much less than the thermal energy emitted by a blackbody at ground air temperature in this wavelength range. Hence, a surface on the earth facing the sky experiences an imbalance of outgoing and incoming thermal radiation and cools to below the ambient air temperature [1,2]. While this concept can work well at night, assuming a relativity dry atmosphere, the solar energy input during day, which is normally much greater than the radiated out, causes heating of the system. To prevent this, a shield is needed to cover the radiating surface in order to block solar radiation during the day as well as to prevent convective mixing in the cooled space.

For this reason, a shield is required that serves the dual purpose of preventing the solar radiation from reaching the radiator and preventing convection between the radiator and the ambient, but allow complete transmission in the “atmospheric-window” region. Infrared radiation (8–13 μm) should preferably be transmitted, as any absorbed radiation will be converted to heat somewhere in the system.

Cadmium sulphide films have been grown by a variety of techniques, such as chemical vapor deposition, chemical bath deposition (CBD) and chemical solution deposition (CSD). Among these techniques, the latter appears promising for the design of radiative cooling shield [3] and is suitable for the preparation of large-area thin films [4,5].

For this paper, we discuss cadmium sulphide thin film and their optical properties in order to assess the possibility of the CdS thin film for radiative cooling uses. So, our aim is to investigate different approaches for design of the shield for radiative cooling; focusing on film deposition by CSD method, with emphasis on their optical properties as a shield for passive cooling devices.
2. Experimental

2.1. Sample preparation

The processes of substrate treatment were as follows: firstly, the substrate was dipped in isopropyl alcohol, acetone, and carbon tetrachloride; secondly, it was rinsed with distilled water after dipping; finally, the substrate was dried.

Details of the deposition of CdS by CSD technique are widely described in the literature [6,7]. In short, trisodium citrate (TSC) was used as complexing agent. Aqueous stock solution of 0.2 M CdCl₂ and a 0.01 M of Na₂S₂O₃ was used. The pH of the aqueous solution is adjusted to pH 2.2 and the temperature of the bath is maintained neighbour of 90 °C to have a very low deposition. The silicon substrate was placed in the solutions for typically 24 h periods. The thin layer of CdS has been deposited for a cathodic potential equal to −0.6 V [6]. In this manner, CdS is deposited in the form of transparent, uniform and adherent film. Based on deposition time, the average thickness of the film CdS is about 1 mm. The cathodic reactions that drive deposition in the form of transparent, uniform and adherent film. Based on deposition time, the average thickness of the film CdS is about 1 mm. The cathodic reactions that drive the simultaneous deposition of the cadmium and sulphur are as follows:

\[
\begin{align*}
\text{Cd}^{2+} + 2e^- & \leftrightarrow \text{Cd} \\
\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 4e^- & \leftrightarrow 2\text{S} + 3\text{H}_2\text{O}
\end{align*}
\]

2.2. Experimental instrument

Spectral specular reflectance and transmittance measurements are made over the full (0.3–20 μm) using an OL-750 spectroradiometer equipped with a controller [2]. The modular approach of the OL-750 coupled with an extensive selection of accessories and powerful application software packages enables the user to tailor a turn-key system to their requirements as well as ensure repeatability. The system is primary made up by double source: a tungsten filament source was used from 300 nm to 1000 nm and a gloower filament source from 1 μm to 20 μm, which were kept up at a high stability by a stabilized dc power supply.

The inaccuracy in the value of spectral specular reflectance and transmittance is estimated, from repeated measurements on different samples, to be less than 2%. A silicon detector is used for the wavelength range from around 300 to 1000 nm, whereas a pyroelectric detector covers the range between 1 and 20 μm. Under these conditions used here, the spectral resolution was about 0.01 nm. The samples are held in an adjustable mount precisely at the centre of a horizontal ring in a holder, which can rotate around its vertical axis. The detector can be swept around the ring then allowing for measuring the spectral specular reflectance at different angles of incidence. Near normal reflectance was measured at an angle of 1° to decrease the influence of multiple reflections.

2.3. Model for the radiative cooling effect

The model under study is shown in Fig. 1. It is an ideal absorber surface (emitter) put on the earth, covered by a horizontal shield [2,8]. The shield receives radiation in a wide range from the sun and the atmosphere. The solar energy is first absorbed by the shield, which reflects back a part in space and transmits the rest toward the absorber. The absorber emits thermal radiation toward the window which is partially reflected and absorbed by the absorber. At the thermal equilibrium, the window radiates its thermal energy toward the space and absorber according to Lambert’s law (Fig. 1).

The window is characterized at each wavelength by three coefficients measuring the fraction of the incidental spectral power being able to be subjected to the reflection, transmission and absorption. For each wavelength, there are two spectral transmission coefficients \( T_1(\lambda), T_2(\lambda) \) and two spectral reflection coefficients \( R_1(\lambda) \) and \( R_2(\lambda) \) corresponding, respectively, to the waves traveling from the side (1) to the side (2) and from the side (2) to the side (1). The spectral absorption coefficients \( A_1(\lambda) \) and \( A_2(\lambda) \) will be deduced by the difference

\[
A_1(\lambda) + R_1(\lambda) + T_1(\lambda) = 1,
\]

where \( \varepsilon_1(\lambda) \) and \( \varepsilon_2(\lambda) \) are, respectively, the spectral emissivity of the side (1) and the side (2), they can be written according to Kirchhoff law as

\[
\varepsilon_1(\lambda) = A_1(\lambda), \quad \varepsilon_2(\lambda) = A_2(\lambda).
\]

In order to be able to compare the characteristics of optical properties of the shield, we will define some optical functions. We define integrated reflected intensity and integrated transmitted intensity for VIS/NIR and for “atmospheric-window”. We follow the definition of Nilsson et al. [9] for solar band reflectance \( R_{\text{sol}} \) of the film over the entire solar spectral (0.3–2 μm), as given by

\[
R_{\text{sol}} = \int_{\lambda_1}^{\lambda_2} R(\lambda) W(\lambda) d\lambda / \int_{\lambda_1}^{\lambda_2} W(\lambda) d\lambda,
\]

where \( W(\lambda) \) is the solar spectral irradiance power per wavelength interval.
where \( W(\lambda) \) is the standard solar irradiance data \([10,11]\) and \( R(\lambda) \) is the spectral reflectance of the film.

In an equivalent way we calculated the solar band transmittance \( (T_{\text{sol}}) \) and solar band absorption \( (A_{\text{sol}}) \) as given by the following equations

\[
T_{\text{sol}} = \frac{\int_{\lambda_1}^{\lambda_2} T(\lambda) W(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} W(\lambda) d\lambda},
\]

and

\[
A_{\text{sol}} = 1 - (R_{\text{sol}} + T_{\text{sol}}).
\]

Applying the same calculation in the atmospheric-window is a more complex issue, since the sky spectrum (atmospheric-window range) is highly dependent on the humidity of the atmosphere. The structure of the Earth’s atmosphere is complex, and the methods used to model the transport of radiation through it can be equally complicated. The minimum parameters required to characterize the atmosphere for optical modeling and spectral measurements research are turbidity, precipitable water vapor and carbon dioxide \([11–13]\). In this paper, we will use the results of Passman and Larmore giving the atmospheric transmission from the absorption coefficient from \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) \([14]\), and in same way, \( T_{8–13}, R_{8–13} \) and \( A_{8–13} \) are calculated in the atmospheric-window range. The IR band properties are evaluated for a spectral distribution of blackbody at radiance of 300 K.

3. Results and discussion

The spectral specular transmittance, reflectance and absorbance of the CdS thin film (1 mm) are shown in Fig. 2. From spectral specular absorbance, we can see the position of the two critical-points structures at \( E_1^c \) and \( E_2^c \) (0.31 \( \mu \)m, 0.33 \( \mu \)m). The low-energy peak \( (E_1) \) of CdS shows a splitting of 0.01 \( \mu \)m. It’s, therefore, reasonable to identify this peak with transition at a point of \( k \) space between the top of the valence band and the lowest conduction band \([15]\).

The weak structure at \( E_1^c \) and \( E_2^c \) was not visible in every specimen, although when it appeared, the visibility of these very weak peaks is thus presumably critically dependent on the condition of the crystal surface and the quality of the crystal. We observe also sharp absorbance structure due to an intense narrow absorption band at slightly lower wavelength than the optical transmission limit. The interpretation of this band as due to the creation of “direct” excitons is consistent with strain-induced splitting in the reflection spectra and with the linewidth transmission for such excitons \([16]\). The energy difference between the peak exciton absorption and the optical transmission limit sets a rough upper limit of 1–1.2 \( \mu \)m on the difference between the direct and indirect band gaps. It is not know if this limit is consistent with the apparent absence of lifetime broadening of the exciton absorption due to interaction with lower energy bands. The photon energy showed that part or all of this absorption could be due to indirect interband transitions \([17]\).

Optical measurements were carried out using one configuration that the CdS thin film coating facing from the incident beam. The spectral measurements are presented in (Fig. 2). Table 1 gives the above radiative properties for the shield reported in this work.

The solar band reflectance over most of the solar region is rather low \( (R_{\text{sol}} = 0.02) \). As can be seen from Fig. 2, the

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_{\text{sol}} )</th>
<th>( T_{\text{sol}} )</th>
<th>( A_{\text{sol}} )</th>
<th>( T_{8–13} )</th>
<th>( A_{8–13} )</th>
<th>( R_{8–13} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS thin film</td>
<td>0.02</td>
<td>0.3</td>
<td>0.68</td>
<td>0.80</td>
<td>0.19</td>
<td>0.01</td>
</tr>
</tbody>
</table>

![Fig. 2. Spectral specular transmission and reflection of the CdS thin film.](image-url)
solar band transmittance is reasonably very low in \((T_{\text{sol}} = 0.30)\) and falls to a null value in the visible region. The window IR band transmittance is very high \((T_{8-13} = 0.80)\), but the IR band reflectance of the radiative object is very low 0.01 for the 8–13 \(\mu\)m band, that is, the IR band emittance reaches 19%. The concept of this approach is to combine low solar band transmittance from the upper side of the shield and to high transmission in the “atmospheric-window” from the lower side of the shield. The CdS thin film do appear to possess the appropriate properties for use as a shield radiative cooling devices than the CdTe thin film [18]. Such radiative properties values are suitable for passive cooling use [4,19].

In the conditions of a normal incidence \((T = 300 \text{ K})\), the temperature of the black absorber is calculated at 364 K. Using the measured radiative properties (Table 1), the computed temperature of the black absorber when it’s covered by the shield is 299 K [20,21]. The radiative properties of the thin film affect an important cooling effect that the calculated value of the absorber temperature placed below the shield is less than the absorber temperature, when it’s uncovered, with a difference of 65 K.

4. Conclusions

CdS thin film (1 mm) is a good “atmospheric-window material, it have low IR band reflectance (below 0.02) and high IR band transmittance (0.80) across the 8–13 \(\mu\)m band. It would be suitable for preparing radiative cooling object based on spectral reflectivity. Further experimental work on reducing the longer wavelength transmission, increasing the reflectivity and fabricating actual devices using this film is required.

References