

# Thermochromic effect with semiconducting layers



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## ABSTRACT

A switching of reflectivity with temperature can be achieved in the infrared region, using thermally activated charge carriers in a single semiconductive layer on a reflective base material, when the interference effect between front and back side of the layer is used. We outline, how a surprisingly small change in conductivity – of less than an order of magnitude – changes the reflectivity more than 60% when the semiconductive material is tailored to its task regarding its activation energy and charge carrier density. As a proof of principle, titanium oxynitride layers were prepared on aluminum. A change of reflectivity of 21% was achieved when the sample temperature was increased from 25 °C to 150 °C, and a change of 34% when the sample was heated to 250 °C.

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## 1. Introduction

The absorber layers of state of the art collectors for solar thermal systems are optimized to absorb as much sunlight as possible and to minimize the radiative heat loss in the infrared region. This ensures a high efficiency, which is welcome, as long as storage capacity is available, acting as a heat sink for the collector. But when the maximum storage temperature is already reached and the system goes into stagnation, this high efficiency causes the collector to heat up further, resulting in heat spread and significant thermal stress for system components [1]. So it is desirable to lower the collector stagnation temperature as collector materials and system components could be sized for less stressful conditions and the costs for the whole system could be reduced significantly.

It has been suggested to use thermochromic materials to create additional heat loss by switching the infrared emissivity  $\epsilon_{\text{rad}}$  from a low value in the cold state to a high value in the hot state [2]. Layers containing the thermochromic phase change material VO<sub>2</sub> were prepared and analyzed for this reason [3–5] and VO<sub>2</sub>-layers prepared on aluminum achieved changes in reflectivity from about 90% at RT to 55% at 100 °C in the relevant infrared spectral region [6].

However, the basic optical layout of thermochromic absorber layers and how it can be implemented to derive material specifications and optimization routes was not addressed so far. In doing so, we can state concise specific conductivities and layer thicknesses for optimal emissivity switching.

Additionally, these considerations gave us the insight that not only phase change materials but also semiconductive layers have the

potential to solve the problem. We outline the use of this class of material and give first results implementing titanium oxynitride layers.

## 2. Theoretical considerations and layer specification

### 2.1. General specifications

The optical properties of a material in the infrared region are strongly influenced by the possibility of a free charge carrier to move in an electric field and by the decay time of the electric current, i.e. by the specific conductivity  $\sigma$  and the scattering time  $\tau$  of the material. This is described by the well known Drude model, which is based on electron transport in metals [7]. The dielectric function  $\epsilon(\omega)$  based on the Drude model is given by

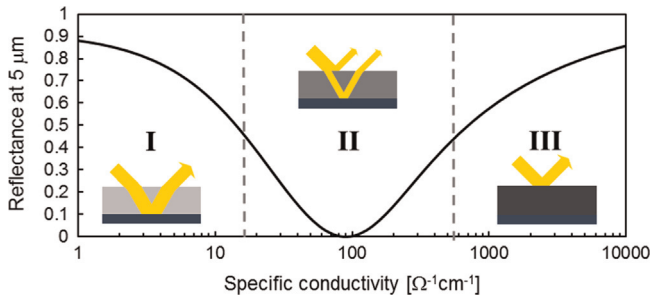
$$\epsilon(\omega) = \frac{\epsilon_{\infty} - \sigma}{\epsilon_0 \cdot 1} (\omega^2 \tau + i\omega) \quad (1)$$

where  $\epsilon_0$  is the dielectric constant,  $\epsilon_{\infty}$  is the dielectric constant offset and  $\omega$  is given by  $\omega = 2\pi/\lambda$ . The optical constants of the material are calculated by  $n + ik = \sqrt{\epsilon}$ . As the conductivity of a material increases, the refractive index  $n$  and the extinction coefficient  $k$  also increase, leading to higher absorption and a higher surface reflectivity and in the end to the excellent reflectivity of metals.

Typically, a solar absorber is made of a metal sheet (Al or Cu) coated with a thin dielectric layer which absorbs solar light but is transparent to infrared light, such as black chromium [8]. The dielectric layer disturbs the infrared metal reflection only marginally, ensuring the high reflectivity and low emissivity of the absorber.

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**Fig. 1.** Reflectivity of a single layer with a quarter wave optical thickness for 5  $\mu\text{m}$  on a metallic substrate ( $n=9$ ,  $k=45$ ) calculated with the Drude model, assuming an offset to the dielectric constant  $\epsilon_{\infty}=5$ , a scattering time  $\tau=0.5$  fs and no residual absorption.

We stay with this simple setup of a single layer on aluminum. But since we want to use interference to achieve a high sensitivity of the absorber towards changes in the coating material, we choose the layer thickness  $d$  to be of quarter wave optical thickness, i.e.  $d=\lambda/(4n)$ , where  $\lambda$  denotes a wavelength in the infrared and  $n$  the refractive index at the respective wavelength. As typical stagnation temperatures of collectors are aimed to stay below 150  $^{\circ}\text{C}$  for the flat panel type or below 250  $^{\circ}\text{C}$  for vacuum tubes, we choose  $\lambda$  to be around 5–7  $\mu\text{m}$ . The reason being, that the maximum of the Planck radiation curve lies within this wavelength region for these temperatures. Therefore, the thickness specification for the absorber layer depends on the desired temperature range. It can be calculated using the refractive index of the material and Wien's displacement law.

In the following text the reflectivity  $\rho_{\text{rad}}(\lambda)$  instead of emissivity  $\epsilon_{\text{rad}}$  is considered, as the former can be more easily accessed by measurements and as emissivity is simply given by  $\epsilon_{\text{rad}}(\lambda) = 1 - \rho_{\text{rad}}(\lambda)$  for intransparent substrates. Fig. 1 shows how the reflectivity of the absorber at 5  $\mu\text{m}$  changes when the conductivity of the single layer is varied. Three regions can be distinguished: In region I the high reflectivity of a dielectric layer on metal can be observed, as already described for the classical absorber. In region II, the conductivity of the layer is increased, leading to absorption within the layer and to enhanced surface reflection at the boundary of the layer to the ambient. Therefore the electric field strength of the two light rays (1) reflected at the layer-ambient interface and (2) reflected at the layer-aluminum interface (and multiple reflections) become comparable. Since an optical thickness of a quarter wave was chosen, the interference is destructive and reflectivity is minimized. In region III the behavior is dominated by the front surface reflection, as the optical constants of the single layer are now already metal-like.

Depending on the starting point, it is possible to either enlarge or reduce reflectivity with increasing conductivity. But in both cases a significant change in reflectivity can be obtained with only small changes in conductivity, if the areas around the inflection points are used. In our case a reduction of reflectivity is desired, so  $\sigma(T_c) < 5 \Omega^{-1} \text{cm}^{-1}$  would be a good value in the cold state and  $50 \Omega^{-1} \text{cm}^{-1} < \sigma(T_h) < 200 \Omega^{-1} \text{cm}^{-1}$  is recommendable for the specific conductivity in hot state at the respective temperatures  $T_c$  and  $T_h$ .

It has to be noted that the optimal conductivity depends on the refractive index and the scattering time of the coating material, and that the given specific conductivity is an "optical" or "Drude" conductivity which can deviate significantly from a conductivity measured by constant current methods like four-point-probe. This is because on one hand, the layers are not perfect, containing grain boundaries, and on the other hand, the scattering time might be a function of frequency. Also, the optimal conductivity will be shifted to slightly higher values when the total emissivity of the

absorber is calculated, as this includes the whole spectral region and the reflection minimum will be broader for higher conductivities.

Now conductivity has to be linked to temperature. It has already been suggested to use  $\text{VO}_2$  as an absorber layer, switching from a semiconductive phase at room temperature to a metallic state above 68  $^{\circ}\text{C}$  [3–6]. But as the change of conductivity in the bulk material is five orders of magnitude [9], the problem arises that the material simply shoots through the minimum. It starts with a high reflectivity in the cold state, goes through the minimum during the switching process and ends at a high reflectivity of over 80% for the bulk material. The conductivity switching of non stoichiometric material or thin layers deviates [10,11] and a lower reflectivity of 55% was achieved in the hot state in [6] for example. However, it is very limiting to consider only one material.

Therefore we propose to use the comparatively weak effect of temperature dependent activation of free charge carriers. This opens up a whole new class of materials which can be tuned in their behavior. In the next section we will derive the necessary material specification.

## 2.2. Specifications for semiconductive layers

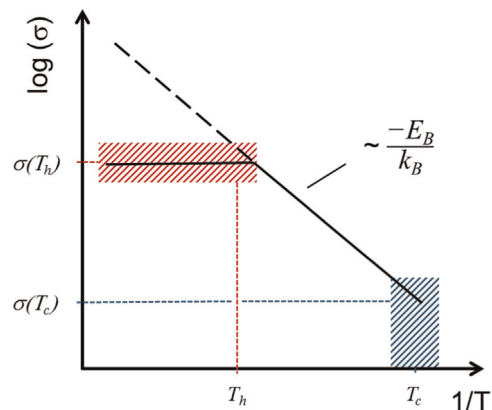
The formalism for charge carriers that have to be activated by temperature  $T$  across an energy barrier  $E_B$  is already well known from semiconductor science. The general relationship between conductivity, charge carrier mobility  $\mu$  and density  $n_{el}$  is given by Eq. (2), where  $e$  denotes the unit charge. Neglecting – for the sake of simplicity – the temperature dependence of mobility and the density of states  $N$ , we arrive at Eq. (3) where the subscript "0" signifies a mean value and  $k_B$  the Boltzmann constant.

$$\sigma(T) = e \cdot \mu(T) \cdot n_{el}(T) \quad (2)$$

$$\sigma(T) \approx e \cdot \mu_0 \cdot N_0 \cdot \exp(-E_B/(k_B T)) \quad (3)$$

For dopant energy levels  $E_D$  in a semiconductor or a band gap energy  $E_G$  the activation energy  $E_B$  has to be substituted by  $E_D/2$  or  $E_G/2$ . But as the concept discussed here has a broader scope, the more general activation energy  $E_B$  will be used.

The necessary activation energy  $E_B$  can now be easily derived from the gradient, connecting the optimal conductivity in hot and cold state, if the logarithm of conductivity is plotted versus  $1/T$ . This is illustrated in Fig. 2. The target regions for the conductivity in hot and cold state are marked as shaded areas. The conductivity in the cold state can extend to even lower values, but to derive the



**Fig. 2.** Schematic diagram of thermally activated conductivity. The target regions for conductivity in hot and cold state are marked by the shaded areas. The continuous line corresponds to an extrinsic semiconductor that reaches its saturation conductivity in the hot target region. An intrinsic semiconductor would show increasing conductivity along the dotted line with increasing temperature.

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