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Estimation of the porosity and refractive index of sol–gel silica films using high resolution electron microscopy

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ABSTRACT

The relationship between the refractive index and the porosity of silica based anti-reflective coatings (ARCs) has been studied. The coatings were prepared with the traditional Stöber method. The refractive index was evaluated by fitting vis–NIR transmittance spectra to Fresnel's coefficient of reflection using the transfer matrix method. The porosity was assessed by a novel method based on image processing of high resolution scanning electron microscope (SEM) images. Results were compared to the commonly used Yoldas and Maxwell–Garnett mixing rules. Our results showed better agreement with the Yoldas mixing rule than with the Maxwell–Garnett mixing rule, which was explained as being due to the presence of elongated crack shaped pores in the ARCs rather than randomly dispersed spherical shaped pores, as was evident in the SEM images. Furthermore, we found that despite the presence of the elongated cracks, the coating appears to behave towards light like a homogenous medium. This somewhat surprising result calls for further research. Lastly, we have shown that it is reasonable to assume that the ARC is vertically homogeneous in terms of its porosity and effective refractive index.

1. Theoretical background

1.1. The importance of ARCs

Anti-reflective coatings (ARCs) are a very common component of a wide range of applications, including photolithography [1], electronic screens [2], and solar cells [3]. A thorough review of the topic can be found in Raut et al. [4]. These authors survey the theoretical basis of ARCs, along with numerous applications and preparation methods. Interestingly, they note that a large part of current and future research in ARCs relates to solar applications. This trend can be attributed to the endless quest for improving the efficacy of solar receivers [4]. In this work, we will take the perspective of the solar industry, but the conclusions are equally valid for all other ARC applications.

1.2. The parameters controlling the transmittance of an ARC containing system

As understanding the parameters controlling the transmittance through a transparent glass slide coated on both sides with an ARC is not trivial, we explain here some of the theoretical principles behind the behavior of light in the system and its computation.

Whenever light is incident on a single interface between two media, a fraction is reflected back. Fresnel's reflection coefficient (FRC) may be used to calculate the fraction of reflected light, both in terms of the magnitude of the electric field of the light and in terms of the intensity or power. Assuming that the incident light is monochromatic, unpolarized, and incident normal to the interface, and assuming a smooth interface between two homogenous media, the FRC for the electric field is,

$$r = \frac{n_1 - n_2}{n_1 + n_2} \tag{1}$$

Eq. (1) – Fresnel's coefficient of reflection (FRC) for unpolarized light incident normal to a smooth interface between two homogeneous media of refractive index n_1 and n_2, respectively.

The fraction of the intensity or power reflected (the reflectance) is then given by $R = |r|^2$.

Further assuming no losses, the fraction of the intensity or power transmitted (the transmittance) is given by $T = 1 - R$ [5].

A layer of material presents two or more interfaces, and light that enters a layer will reflect back and forth internally inside of the layer, undergoing constructive and destructive interference as a function of the thickness of the layer. However, in the case of a thick layer of glass (~1 mm thickness), small variations in the thickness that result from the typical manufacturing process tend to wash out the coherency of the constructive and destructive

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interference of the light, and the reflectance and transmittance for a lossless thick glass layer surrounded on both sides by air or vacuum may generally be written as [6],

$$R = \frac{1-2n_{glass}}{1+n_{glass}^2}$$

$$T = 1 - R = \frac{2n_{glass}}{1+n_{glass}^2}, \tag{2}$$

Eq. (2) – The reflectance and transmittance for a thick glass slide in an air or vacuum environment, where n_{glass} is the refractive index of glass, and the refractive index of air or vacuum is set as 1.

In the case of an ARC, on the other hand, the constructive and destructive interference generally must be considered as a function of the thickness of the ARC. A convenient method for describing the reflectance and transmittance through an ARC, and especially through a sequence of layers including ARCs, is the transfer matrix method (TMM). A detailed discussion of the TMM has been published by Katsidis and Siapkas [7]; we present here only the details relevant to the current study. In the TMM, the reflection at each interface (for normally incident light) is described by an interface matrix,

$$M_{interface} = \frac{1}{1-r}\begin{pmatrix} 1 & r \\ r & 1 \end{pmatrix} \tag{3}$$

Eq. (3) – The matrix representing the behavior of light at an interface between two media when the light is incident normal to the interface. r is Fresnel's coefficient of reflection as defined in Eq. (1).and the propagation of the light through each layer in which coherent constructive and destructive interference of light occurs is described by a propagation matrix,

$$M_{propagation} = \begin{pmatrix} \exp(-jk_0nl) & 0 \\ 0 & \exp(jk_0nl) \end{pmatrix} \tag{4}$$

Eq. (4) – The propagation matrix representing the behavior of light when propagating in a medium. j is the square root of -1, k_0 is the wavenumber of the light in vacuum, n is the refractive index of the layer medium with respect to vacuum, and l is the thickness of the layer.

These matrices are multiplied in sequence to create the total matrix for a system of layers with interfaces, M_{total}, and the reflectance and transmittance for the entire system are given by,

$$R = \left|\frac{M_{total}(2,1)}{M_{total}(1,1)}\right|^2.$$

$$T = \left|\frac{1}{M_{total}(1,1)}\right|^2 \tag{5}$$

Eq. (5) – The reflectance and transmittance as calculated from the TMM, where R is the reflectance, T is the transmittance, and $M_{total}(2,1)$ and $M_{total}(2,1)$ are elements of the total matrix representing the system.

In the case of a system combining coherent and incoherent layers, the calculation is more involved. Katsidis and Siapkas [7] suggest a two-step calculation. In the first step, the conventional TMM described above is used to calculate the reflectance and transmittance of light through the sequence of coherent layers that precede a given incoherent layer (in the direction of propagation of the incident light), and then again to calculate the reflectance and transmittance of the sequence of coherent layers that follow the incoherent layer. This creates two coherent blocks surrounding each incoherent layer. In the second step, the coherent blocks are combined with the incoherent layer assuming no constructive or destructive interference in the incoherent layer, and the total transmittance is given by,

$$T_{total} = \frac{T_{layers\ preceding}T_{layers\ following}}{1-R_{layers\ preceding}R_{layers\ following}} \tag{6}$$

Eq. (6) – The total transmittance through a combined system containing coherent and incoherent layers, based on Katsidis and Siapkas [7], where $T_{layers\ preceding}$ and $R_{layers\ preceding}$ are the transmittance and reflectance, respectively, of the block of coherent layers that precedes the incoherent layer, and $T_{layers\ following}$ and $R_{layers\ following}$ are the transmittance and reflectance, respectively, of the block of coherent layers that follows the incoherent layer.

As can be seen from the equations above, the two characteristics of an ARC that affect the reflectance of the system are its refractive index (RI; n) and its thickness (l). Hence, controlling these qualities is key for productive ARC preparation. In the current work, we focus on the RI of the ARC.

1.3. Parameters controlling the RI

As is well known in the field of ARC design, the ideal ARC will have an RI equal to the geometric average of the RIs of air and glass ($\sim$1.23 [8]), which is lower than the RI of any typical material. Therefore, the effective RI of ARCs is typically decreased from the RI of the bulk ARC material by introducing porosity to the ARC layer or by patterning the layer's surface [4]. In essence, these two approaches are based on the same principle, namely exploiting the low RI of air to reduce the effective RI of the layer. Thus, understanding the relationship between the RI and porosity is pivotal for realizing a better ARC.

1.4. Mixing rules

1.4.1. Mixing rules – general

Many different formulas, called “mixing rules” or “effective medium approximations” (EMAs), exist for predicting the effective RI of a mixture of two materials, such as silica and air. An insightful review of the topic can be found in Sahoo et al [9]. These authors survey the interrelationship among the different mixing rules and the conditions upon which each is valid, focusing on the application of thin optical coatings. In general, mixing rules vary in their assumptions, and it is not always obvious which mixing rule is most appropriate for calculating the effective RI of an ARC. In addition, the premise of mixing rules is that the mixture behaves towards incident light as a homogeneous large medium would, i.e., that the light is reflected, refracted (in the case of non-normal incidence), and transmitted, without net scattering in other directions caused by the “irregularities” (in the case of a porous material, the pores or the material between the pores are the irregularities). Such a premise should be valid only when the irregularities are significantly smaller than the wavelength of the light inside of the layer [9,10] and when they are randomly dispersed throughout the layer. (Even when the irregularities are significantly smaller than the wavelength of the light inside of the layer, the irregularities scatter the light into all directions. However, such scattering may be considered dipole scattering, and in the context of mixing rules, this dipole scattering becomes incorporated into the average dipole moment of the material and ultimately into its effective RI [11].)

For solar cell applications, the incident light is solar radiation arriving at the surface of Earth. The specific intensity (intensity per wavelength interval) of solar radiation at the Earth's surface according to the dataset “Air Mass 1.5” [12] has a maximum at $\sim$530-nm wavelength. Dividing 530 nm by the RI of the ARC ($\sim$1.23), the wavelength of the light inside of the ARC layer will be $\sim$430 nm. Therefore, the pores should have a diameter