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Colored solar selective absorbing coatings with metal Ti and dielectric AlN multilayer structure

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ABSTRACT

The colored solar–thermal collectors have the advantages of architectural integration and color appearance. The solar selective absorbing coatings with a metal–dielectric multilayer structure can show different colors by changing the layer number and thickness. In this work, five colored coatings with a metal titanium (Ti) and dielectric aluminum nitride (AlN) multilayer structure were designed by the optical multilayer software and fabricated by magnetron sputtering. The color of the five coatings is black, purple, yellowish green, red, and yellowish orange. The energy performance, chromaticity, and brightness of the coatings were studied and compared. The results show that the solar absorbance of these coatings is between 0.82 and 0.94, the thermal emittance is between 0.05 and 0.27, and the brightness is in the range of 0.65–8.89%. These colored coatings can be produced by a commercial production process, and is suitable for the application of building integration.

1. Introduction

Solar–thermal collectors with high absorbance and low thermal emittance have been used for converting solar energy into thermal energy [1,2]. The collector absorbing surface is usually black in order to maximize the absorption of the solar spectrum. However, the black color of the collectors on building roofs and facades limits the architectural integration into buildings [3–6]. Moreover, a survey presents that 85% of architects would prefer colored solar collectors other than black ones [4,7,8]. Therefore, it is important to fabricate colored collectors with high solar–thermal conversion efficiency.

Previously, several methods have been proposed to fabricate colored collectors, such as spectrally selective colored paint [5,6], colored glazed collectors based on thin film interference filters [7,9–12], and colored absorbing coatings [8,13]. Amongst these, the colored absorbing coatings have the advantages of a good thermal stability and a low cost in production.

Both wet chemical methods [14,15] and physical vapor deposition [2,8,16] have been used to prepare solar selective coatings. Based on physical vapor deposition, the magnetron sputtering technique is widely used to produce the absorbing coatings with a metal–dielectric composited structure [2], owing to the good chemical and thermal stabilities of its products. Accordingly, the solar selective coatings with a metal–dielectric multilayer structure were also prepared by the magnetron sputtering method [17–19], which has the advantages of good reproducibility, spectral stability in the deposition process, and satisfying the commercial requirements of a mass production process [18,19]. However, a systematic research about the colored absorbing coating with a metal–dielectric multilayer structure still remains to be reported.

In this work, the colored solar selective absorbing coatings with a metal–dielectric multilayer structure were designed by the optical multilayer design software and fabricated by the magnetron sputtering technique. The optical constants of metal titanium (Ti) and dielectric aluminum nitride (AlN) films with different thicknesses were retrieved from the reflectance or transmittance values. Energy performance, chromaticity, and brightness of the colored coatings were studied.

2. Experimental details

In order to obtain the optical constants of AlN and Ti single layer films, dielectric AlN films with different thicknesses were deposited on quartz substrates using a metal Al target (99.99% in purity) by the reactive dc magnetron sputtering. Accordingly, metal Ti films with different thicknesses were deposited using a metal Ti target (99.99% in purity) by the non-reactive dc magnetron sputtering. The substrates, 0.5 mm thick, 2.5 cm $\times$ 2.5 cm, were cleaned in acetone and ethanol several times before deposition. The distance between the substrate and target was 13 cm. The base pressure of the vacuum chamber was 4.0×10^{-4} Pa and the sputtering power was 100 W. The thickness of the film was controlled by the sputtering

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time according to the deposition rate. Before the deposition of Ti–AlN multilayer coatings, a Cu layer with thickness about 120 nm was deposited on quartz substrate using a metal Cu target (99.99% in purity) by the dc magnetron sputtering. The deposition parameters of Cu, Ti, and AlN layers are summarized in Table 1. Five colored solar absorbing coatings with a Ti–AlN multilayer structure were prepared, and the Ti and AlN layers were deposited at the above conditions. The color of the coatings is black, purple, yellowish green, red, and yellowish orange.

The normal incidence transmittance (T) and total reflectance (R) of the samples were recorded in the wavelength range of 300–2500 nm with a spectral resolution of 1.0 nm by a double-beam spectrophotometer (Perkin-Elmer Lambda 950). It was equipped with an integrating sphere for measurements of total R. Infrared spectra were acquired with a Perkin-Elmer Spectrum One Fourier transform infrared (FTIR) spectrophotometer in the range of 2.5–25 μm (4000–400 cm^{-1}). FTIR spectra were measured with a 10° specular reflectance accessory and a gold substrate alignment mirror at room temperature and the spectral resolution is about 0.9 cm^{-1}.

3. Optical constant deduction

Many methods for the determination of optical constants have been reported [20–28]. Generally, the optical constants of a film were retrieved by simulating the experimental ellipsometric spectra [21–24], transmittance or reflectance [25–28] based on the optical dielectric models. We have determined the optical constants and thickness of an In_2O_3:Sn film from transmittance data based on the Forouhi–Bloomer model combined with the modified Drude model in our previous research results [26]. In this research, Ti film is a metal film and AlN is a dielectric film. Therefore, the optical constants of AlN film were calculated by the Forouhi–Bloomer model combined with the modified Drude model [26,27]. For the Ti film, the Drude–Lorentz model was used to determine the optical constants, which combines the Drude model with the Lorentz oscillator model. The dielectric function of the Drude–Lorentz model can be expressed as [24,28]

$$\varepsilon_{DL}(\omega) = \varepsilon_b - \frac{\omega_D^2}{\omega^2 - i\gamma_D\omega} + \sum_j \frac{C_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega} \tag{1}$$

where ω is the frequency, and the constant (ε_b) depends on the contribution to the dielectric constants beyond the simulated spectral range. The second part in Eq. (1) stands for the contribution of the Drude model, where ω_D in Eq. (1) is the plasma frequency and γ_D is the Drude damping constant. The last part is the Lorentz model, where ω_j and γ_j are the frequency and damping terms of a particular resonance line, and C_j is the amplitude of this resonance line.

Based on the optical dielectric models, two computer programs were written in FORTRAN for calculating the optical constants and thicknesses of the metal film and dielectric film using a nonlinear least squares arithmetic. As a result, the optical constants and thickness of AlN film were calculated from the measured transmittance data, and those of Ti film were calculated from the measured reflectance and transmittance data.

Table 1
Sputtering parameters for the depositions of Cu, Ti, and AlN layers.

Layer	Ar flow rate (sccm)	N_2 flow rate (sccm)	Thickness (nm)	Sputtering pressure (Pa)
Cu	42.5	–	120	0.7
Ti	42.5	–	18, 24, 31	0.7
AlN	40	8	63, 85, 265	1.6

4. Energy performance, chromaticity, and brightness

4.1. Energy performance

The energy performance of a solar selective absorbing coating is expressed by two basic parameters of solar absorbance (α) and thermal emittance (ε), when transmittance is zero, which can be calculated by [14]

$$\alpha = \frac{\int_{0.3}^{2.5}(1-R(\lambda))I_s(\lambda)d\lambda}{\int_{0.3}^{2.5} I_s(\lambda)d\lambda} \tag{2}$$

$$\varepsilon = \frac{\int_{2.5}^{25}(1-R(\lambda))I_b(\lambda,\ t)d\lambda}{\int_{2.5}^{25} I_b(\lambda,\ t)d\lambda} \tag{3}$$

where λ is the wavelength (integral borders in μm), $R(\lambda)$ is the reflectance at λ, $I_s(\lambda)$ is the solar spectral radiation at AM=1.5, and $I_b(\lambda,t)$ is the black body spectral radiation, t=80 °C is used for the normal temperature solar–thermal application. Note that the upper integral borders of 25 μm (α) and 2.5 μm (ε) are due to limitations in the spectrometers, and hence do not cover the whole solar radiation spectrum and infrared spectrum, where ideally the upper borders should have been 3 μm and 50 μm (or even 100 μm), respectively.

4.2. Chromaticity

According to the description of the XYZ color system by the International Commission on Illumination (CIE) in 1931, the tristimulus values X, Y and Z are computed from the measured or simulated spectral power distribution data $P(\lambda)$ by [7,8,27]

$$X = \int_{380}^{780} P(\lambda)\bar{x}(\lambda)d\lambda \tag{4}$$

$$Y = \int_{380}^{780} P(\lambda)\bar{y}(\lambda)d\lambda \tag{5}$$

$$Z = \int_{380}^{780} P(\lambda)\bar{z}(\lambda)d\lambda \tag{6}$$

where λ is the wavelength (integral borders in nm). $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ are the CIE-1931 standard spectrum tristimulus values. In this work, $P(\lambda) = D_{65}(\lambda)R(\lambda)$, where D_{65} is a standard illuminant and represents typical daylight. Then the color coordinates x, y, and z are calculated by

$$x = \frac{X}{X+Y+Z} \tag{7}$$

$$y = \frac{Y}{X+Y+Z} \tag{8}$$

$$z = 1-(x+y) \tag{9}$$

4.3. Brightness

When a surface appears to the human eye under certain illumination conditions, the brightness is determined by its visible reflectance R_{VIS}, and can be written as [7,10,27]

$$R_{VIS} = \frac{\int_{0.4}^{0.7} R(\lambda)I_{ILL}(\lambda)V(\lambda)d\lambda}{\int_{0.4}^{0.7} I_{ILL}(\lambda)V(\lambda)d\lambda} \tag{10}$$

where $I_{ILL}(\lambda)$ is the illuminant at λ (integral borders given in μm), and $V(\lambda)$ is the photopic luminous efficiency function.