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THE PHYSICAL PROPERTIES OF FLUORINE-DOPED TINDIOXIDE COATINGS FOR SOLAR COLLECTORS

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ABSTRACT

Fluorine-doped tindioxide layers were produced by pyrolysis. Investigators of the optical and electrical properties show that the spectral selectivity is determined by the electron density n_e and the electron mobility μ . From measurements of mobility as a function of temperature it is shown that the process limiting the mobility will be impurity scattering if the mobility is high, while a low mobility is attributed to grain boundary scattering. This has been confirmed by Scanning Electron Micrography. As a best result a thermal emissivity of 0.15 has been achieved.

KEYWORDS

Spectral-selective layer; tin oxide; pyrolysis; electrical properties; electron scattering; grain-boundaries; emissivity.

INTRODUCTION

Tindioxide layers are electrically conducting and infrared reflecting coatings with a wide range of applications. In the field of solar energy conversion they can be used as a conducting anti-reflection electrode for photovoltaic cells or as a spectrally selective layer for photothermal conversion.

Tindioxide acts as a spectral window. Light is transmitted in the wavelength region confined by λ_{gap} and λ_{plasma} . Below λ_{gap} band gap absorption occurs, above λ_{p} reflection due to free electron plasma behaviour takes place. As most of the solar spectrum is in the 0.3 - 2.0 μm region and thermal radiation is in the infrared above 2 μm λ_{p} should preferably have a value of $\sim 2 \mu\text{m}$. This can be achieved by suitably doping the tindioxide with antimony or fluorine, which enhances the metal character of the layer.

The spectrally selective layer can be applied on the glass cover of a solar energy collector or directly on the absorber surface. Tindioxide layers are mechanically and chemically highly stable, also at high temperatures, and can be produced in a relatively cheap and simple way by spray

pyrolysis (Simonis, 1979, 1987; Karlsson, 1985; Haitjema, 1987).

The major problem when producing tin oxide layers is a relatively high emissivity, which is related to a limited electrical conduction in the layer. In this paper the cause of this limited conductivity is more thoroughly studied and the results of optimizing the spectral-selective properties will be presented.

PREPARATION

The coatings are produced by a spray pyrolysis method as described in an earlier paper (Haitjema, 1987). We used three different spray solutions:

1. a solution of SnCl_4 in alcohol with NH_4F as a dopant
2. a solution of $(\text{C}_4\text{H}_9)_2\text{SnO}$ in acetic acid with CF_3COOH as a dopant (de Jong, 1980)
3. a solution of $(\text{C}_4\text{H}_9)_3\text{SnF}_3$ ($\text{C}_2\text{H}_5\text{O}_2$)

To obtain layers of 0.6 μm thickness or more on window glass or pyrex the substrate is heated and sprayed several times to minimise a large temperature fall during spraying. If spraying is carried out on black enamelled steel (de Jong, 1978) the substrate can be heated to a higher temperature and the coating can be deposited in one go.

MEASURING TECHNIQUES

Reflectance and transmittance in the 0.3 - 2.5 μm region are measured with a Perkin-Elmer Lambda 9 Spectrophotometer, which is equipped with an integrating sphere. The reflectance in the infrared region (2.5 - 50 μm) is measured with a Perkin-Elmer 883 IR-Spectrophotometer with a specular reflectance attachment. The quantities important for solar energy application, thermal emittance ϵ and solar absorptance α , are measured separately with apparatus as described by van der Ley (van der Ley, 1979).

The electrical properties, resistivity and Hall coefficient, are measured according to the van der Pauw method (van der Pauw, 1958) using circular-shaped samples in a 0.6 T magnetic field. A sample holder is used which enables the sample temperature to be varied between 77 and 600 K in vacuum.

Layer thickness is usually calculated from the optical extrema using a method described in an earlier paper (Haitjema, 1987). When the layer thickness is less than about 100 μm a Tencor alphasstep 2000 stylus apparatus is used. In that case a step is made by etching the coating with Zn powder and HCl.

THE DRUDE THEORY

The Drude model, which was originally derived for metals, can be used to relate the optical properties to the electrical properties. On the basis of this model calculations on hypothetical layers have been carried out (Simonis, 1987) which show that the electron density n determines the wavelength at which the transition from minimum to maximum occurs. When the electron density is fixed the IR reflectance is determined by the electron mobility μ . Both results are depicted in Fig. 1. Figure 1. shows that n should be about $3.5 \cdot 10^{20} \text{ m}^{-3}$ and μ as high as possible, preferably above $40 \text{ cm}^2/\text{Vs}$.

The validity of this model has been tested by comparing measured values of the complex refractive index with the values calculated from the electrical measurements (Haitjema, 1987). This comparison showed that the Drude

Fig. 1 Reflectances according to the Drude Theory

theory can well be used to predict the reflectance for wavelengths $> 3 \mu\text{m}$ and hence the thermal emittance. As reducing the emittance is the major problem when producing tin dioxide coatings it is important to investigate the scatter-mechanisms which limit the mobility.

MOBILITY

Samples of different mobility have been produced by spraying tin oxide coatings of different substrate temperatures. The mobility of three samples having low, average and high mobility respectively has been measured as a fraction of temperature. The results are shown in Fig. 2. In this figure we see

Fig. 2 Temperature dependence of mobility

that when the mobility is low it increases with temperature, while when the mobility is high it decreases with temperature. This different behaviour can be explained if we consider the various scattering mechanisms that are operative to determine the measured mobility. The effective mobility μ_F is given by (Kohle, 1986; Stapinski, 1984)

$$\frac{1}{\mu_F} = \frac{1}{\mu_c} + \frac{1}{\mu_l} + \frac{1}{\mu_{gb}} \quad (1)$$

where μ_c takes into account temperature-independent scattering of neutral and ionised impurities, μ_l is due to lattice scattering $\mu_l \sim T$ and μ_{gb} accounts for grain boundary scattering and can be written as $\mu_{gb} = \mu_0 \exp(-\phi/kT)$ where ϕ is the inter grain barrier height. Now the different behaviour in Fig. 2 can be explained as follows. When the mobility is high, the grain boundaries have little influence so the mobility is mainly determined by impurity scattering and lattice scattering, resulting in a decrease of the mobility with temperature. An increase of μ_p with temperature, which occurs when the mobility is low, can only be explained by grain boundary scattering. In this case μ_l and μ_c are less important and will have about the same values as in the case of high mobility. So if a high mobility is desired, first the influence of grain boundaries has to be minimised. Further improvement might be achieved by minimising the number of neutral impurities in the the layer.

SCANNING ELECTRON MICROSCOPY

SEM-pictures have been taken of the samples sprayed at different temperatures. Two of them are shown in Fig. 3. These pictures confirm the

Substrate temperature 500 °C
 $\mu = 3.5 \text{ cm}^2/\text{V}_s$

Substrate temperature 600 °C
 $\mu = 21 \text{ cm}^2/\text{V}_s$

dependence of grain size and mobility with spraying temperature, which is shown by the larger roughness of the sample sprayed at 600 °C ($\mu = 21 \text{ cm}^2/\text{V}_s$) compared to the sample sprayed at 500 °C ($\mu = 3.5 \text{ cm}^2/\text{V}_s$).

RESULTS OF OPTIMIZING

We optimised the Fluorine-doping (to obtain $n_- = 3.5 \cdot 10^{26}/\text{m}^2$) and also the substrate temperature during spraying (to make μ as high as possible). Results are obtained as shown in table 1. The substrate temperature must be high because during spraying the substrate temperature may drop up to hundred °C. On the other hand window glass cannot be heated above 600 °C because weakening occurs at higher temperatures.

TABLE 1. Results of optimizing

Substrate	spray solution	T_s (°C)	ϵ_h	α	d (μm)	$n_{\text{—}}$ ($\cdot 10^{26}/\text{m}^3$)	μ (cm^2/V_s)
Glass	1	600	0.19	0.90	0.50	3.2	35
Pyrex	1	640	0.17	0.91	0.62	2.7	42
Pyrex	3	600	0.15	0.90	0.60	3.5	45
Black Enamel	2	740	0.15	0.91	0.68	3.5	45

(T_s is the substrate temperature, ϵ_h is the total hemispherical emissivity, α is the solar absorption coefficient and d is the layer thickness).

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