



## Correlation between structure and optical properties in low emissivity coatings for solar thermal collectors

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### ABSTRACT

We have investigated the relation between the structure and morphology of TiN coatings with their optical properties. Samples were deposited by magnetron sputtering and, by changing the deposition parameters, different textures and chemical compositions can be obtained as measured by X-ray diffraction and glow discharge optical emission spectroscopy respectively. The transmittance in the visible range, measured by spectroscopic ellipsometry, and the emittance, derived from reflectance in the far infrared range as measured by Fourier Transform Infrared Spectroscopy have been related to the nitrogen atomic content and the preferred crystalline orientations present in the TiN coatings. The visible transmittance of the coatings was found not to be dependent on the preferential orientation, while the emittance clearly improves with increasing the film thickness and the presence of both (111) and (200) crystal orientations.

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### 1. Introduction

The transparent cover of the solar thermal collectors usually undergoes heat losses from the inner side to the exterior and, hence, reduces the efficiency of the device. In order to overcome such a problem, an optimisation of the cover (typically float glass) can be obtained by the deposition of low-emissivity (low-e) coatings. The low-e films are commonly classified into two groups: i) multi-layer coatings [1], which use noble metals (i.e. Ag) as functional layer deposited off-line and ii) monolayer coatings [2], which commonly use SnO<sub>2</sub> films as functional layer that can be directly prepared on the glass production line. These two types of low emissivity coating have distinct pros and cons. The multilayer coatings have high visible transmission ( $T > 80\%$ ), which is not disturbed by interference effects. The presence of a thin noble metal film firstly limits the stability of the configuration to the extent that they can only be used in sealed window spaces [3] and, secondly, increases the production costs of these coatings. The monolayers coatings, in contrast, are relatively cheaper than the multilayer coatings but are inferior in low emission performance as they are thicker and the visible transmission is therefore distorted by interferences. The stability, on the other hand, is excellent and this kind of coating can be used in non-sealed windows and even on the exterior glass surfaces.

As an alternative to the noble metals in the multilayer type of coating, transition metal nitrides (TiN, ZrN and HfN) have been used [4]. The primary advantage with this alternative would be improved stability, since the diffusion is much smaller for transition metal compounds than for the noble metals. In particular, TiN films have been proposed as a low-e glass coating [5] due to its good mechanical properties, thermally stability and low electrical resistivity. Besides, controlling the preparation condition, certain visible transmittance and high reflectance of medium-far infrared can be achieved for de TiN coating. TiN films have been extensively studied in order to utilize its high mechanical hardness, high corrosion resistance, low frictional constant and thermodynamic stability [6,7]. Recently, TiN thin films have been studied for further applications as optical coatings, antireflection coatings and antistatic coatings [8]. The optical selectivity of thin TiN films has been experimentally verified but it proved to be a major technical difficulty to prepare thin TiN films with bulk optical properties [9]. TiN films can be deposited by physical vapour deposition (PVD) processes as magnetron sputtering [10] and ion plating [11] or by chemical vapour deposition (CVD) [12]. It has been recently reported [5] that CVD-grown TiN films with (200) preferential orientation present a lower emittance of 0.2 and they are promising candidates for low-e coatings. However, it is well known that in TiN coatings deposited by PVD processes the most common observed growth orientation is (111), although it may change with growth conditions [13]. Despite the many studies performed on the improvement of TiN coatings in low-e applications, it is not clearly elucidated yet the relationships between deposition parameters, film structure and optical response.

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In this work, we have investigated the relation between the structure and morphology of TiN coatings, deposited by magnetron sputtering, with their optical properties.

## 2. Experimental details

Titanium nitride coatings were deposited by reactive magnetron sputtering on single-crystal Si (100) wafers. The Titanium target used is a commercial target of purity 99.995%. A mixture of Ar (99.999%) and N<sub>2</sub> (99.9992%) gases was introduced in the vacuum chamber. The N<sub>2</sub> gas concentration in the reactive atmosphere was varied in the range 1–40% keeping constant the total gas flow (Ar + N<sub>2</sub>) at 30 sccm. In all deposition processes the cathode power was maintained at 100 W.

The deposition set-up consists in a circular planar cathode, 7.5 cm diameter, placed in front of the substrate holder, at a distance of 13 cm. The base pressure of the chamber was  $2 \cdot 10^{-4}$  Pa, approximately and the working pressure was in the range 0.46–0.63 Pa. During the deposition process the substrate temperature was monitored with a thermocouple located on the back of the holder plate. Other details of the sputtering system have been described previously [14]. No intentional heating was made during the deposition process, though the process temperature of the substrates was relatively constant at 90–100 °C. Prior to deposition, 20 min of presputtering have been performed in order to remove the metal-oxide layer of the cathode due to previous deposits. To ensure we were working under the reactive sputtering regime, the samples were grown after the total poisoning of the cathode. The thickness of the TiN films was measured using a mechanical stylus profilometer (Veeco Dektak 150). Crystalline structure was determined by X-ray diffraction (XRD) with grazing incidence mode (angle of incidence 1.5°) using a Cu anode (Cu K<sub>α</sub> = 1.54 Å) at room temperature. The XRD measurements were performed on Siemens D-5000 diffractometer. The chemical composition of the films was determined by glow discharge optical emission spectroscopy (GDOES) using Jobin Yvon RF GD Profiler equipped with a 4 mm diameter anode and operating at a typical radio frequency discharge pressure of 650 Pa and power of 40 W. Spectroscopic Ellipsometry determined the optical properties (refractive index *n* and extinction coefficient, *k*) in the visible range. Measurements were performed on M-2000U ellipsometer working in the range 250–1600 nm and an incidence angle of 70°. The visible Transmittance and Reflectance of the coatings were calculated from *n* and *k* measurements [15]. Reflectance values in the medium and far infrared range (1.5–18 μm) were obtained using a Bruker IFS 60 V Fourier transform infrared spectrometer. The corresponding emissivity (*ε*) values were determined from the experimental infrared reflectance values [16]. According to Kirchhoff's law of radiation, the radiance of film at certain wavelength is equal to the absorption. By applying the equation

$$T(\lambda) + R(\lambda) + A(\lambda) = 1, \quad (1)$$

and assuming that the emissivity is equal to the absorbance *A*, and that normal glass substrate is non-transparent in the region  $\lambda > 4.5 \mu\text{m}$  (*T* = 0), the emissivity can be expressed as:

$$\varepsilon(\lambda) = 1 - R(\lambda). \quad (2)$$

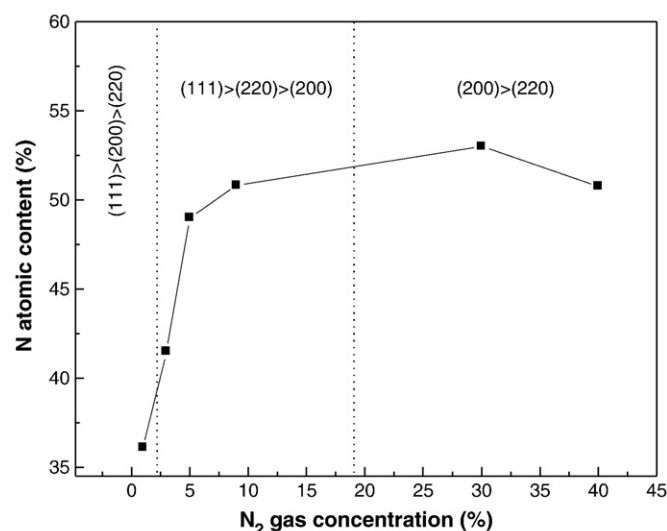
The values of emissivity were calculated from the previous expression for a wavelength of 8 μm, where the reflectance of glass is minimal and emissivity is maximal ( $\varepsilon \sim 1$ ). According to the European standard EN673, the emittance calculated from infrared reflectance experiments (also known as normal emittance) has been corrected (see Table 1).

**Table 1**  
Summary of the transmittance and emittance of the deposited TiN samples.

N <sub>2</sub> gas concentration, %	Thickness, nm	Transmittance (600 nm), %	Emittance (8 μm)
Solar glass		92.0	0.94
1	88 ± 3	1.0	0.20
	149 ± 5	0.1	0.17
3	51 ± 4	23.0	0.82
	105 ± 7	10.0	0.63
	152 ± 3	4.0	0.50
	197 ± 2	1.0	0.34
5	13 ± 2	85.0	0.92
	35 ± 2	39.0	0.86
	111 ± 8	8.0	0.61
9	106 ± 6	11.0	0.62
30	12 ± 3	86.0	0.92
	42 ± 2	31.0	0.80
	63 ± 3	20.0	0.77
	91 ± 6	11.0	0.63
40	13 ± 3	75.0	0.84
	26 ± 2	61.0	0.88
	47 ± 2	29.0	0.66
	56 ± 2	17.0	0.56
	70 ± 6	18.0	0.62

## 3. Results and discussion

In Fig. 1 the nitrogen atomic content incorporated in the coatings versus the N<sub>2</sub> partial concentration in the reactive gas mixture is shown. It can be clearly observed how by increasing nitrogen gas concentration, the nitrogen atomic content in the film rapidly increases. At nitrogen gas concentrations of 1% the nitrogen starts to incorporate into the coating as it has been detected by the GDOES (see Fig. 1). However the nitrogen content in the films is low (about 36%) and stoichiometric films are obtained for nitrogen gas concentrations higher than 9%. In Fig. 2 the effect of the nitrogen gas concentration on the preferential orientation of the TiN thin films with 100 nm thicknesses is shown. For nitrogen gas concentration in the range 1–9%, the preferential orientation present in the TiN films is the (111) cubic phase, although (220) and (200) peaks are already identified in the X-ray patterns. In this range, by increasing the nitrogen gas concentration the TiN (220) orientation increases and the TiN (200) decreases as can be observed in Fig. 2. Although the only phases present in the films correspond to TiN, there is an excess of titanium



**Fig. 1.** Nitrogen atomic concentration in the deposited coatings versus the N<sub>2</sub> partial gas concentration in the reactive gas mixture. The preferential crystal orientations are indicated.

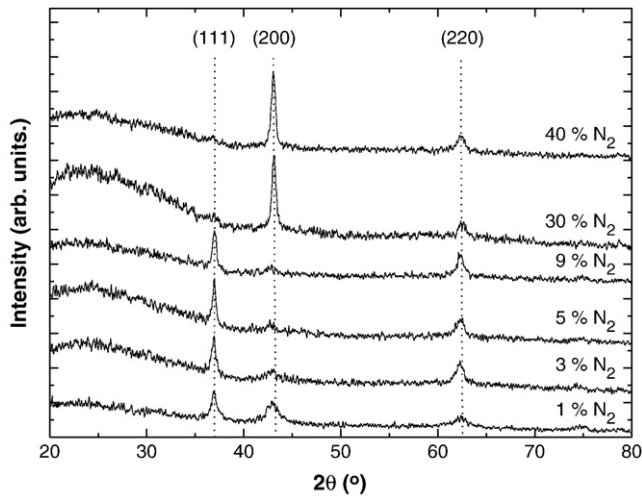


Fig. 2. XRD patterns of the TiN thin films deposited at different the nitrogen gas concentrations (thickness: 100 nm).

content in the films, according to the GDOES results, which is not detected in the diffraction diagrams. Hence, the excess of Ti is supposed to be incorporated in amorphous form or as interstitial atoms in the TiN lattice. For higher nitrogen gas concentrations (30 and 40%) TiN (200) orientation clearly dominates. The (220) orientation is still present while the (111) cubic phase disappears. These experimental results show that the preferential orientation of the TiN films changes from (111) to the (200) plane as the nitrogen gas concentration increases. These changes are related to the optical properties of the coatings as will be discussed below.

The change in the preferred orientation with the film thickness has also been studied. Rickerby et al. [17] observed a trend of the change from (200) to (111) with the film thickness. However, we have found a very different behaviour. For nitrogen gas concentrations lower than 30%, the preferential orientations do not depend on the thickness. For example for samples grown with 30% of nitrogen gas we find that (200) TiN orientation remains preferential within the thickness range studied (10–100 nm) as can be seen in Fig. 3a. Only in the case when the  $N_2$  gas concentration is 40%, the preferential orientation changes with the thickness. At lower thickness (<50 nm), the preferential orientation is (200) TiN. At medium thickness (50–70 nm), there is a competition between (111) and (200) planes, and at the highest studied thickness (100 nm) the preferential orientation returns to (200) TiN (see Fig. 3b). The formation of different preferred orientations during the deposition process can be coupled with the intrinsic stress, which can also induce a considerable amount of strain energy in TiN films [18].

These changes of the preferential orientation with the thickness and the nitrogen content in the TiN coatings have been correlated with the optical properties of the films. In Fig. 4 the variation of the visible transmittance (measured at  $\lambda = 600$  nm) with the thickness for different atomic nitrogen contents is shown. As can be clearly seen the transmittance of the samples deposited with different nitrogen gas concentrations strongly depends on the thickness but not on the preferential orientation.

On the other hand, the emittance calculated from the experimental reflectance values according to the procedure previously mentioned in the experimental section, depends both on thickness and preferential orientation. In Fig. 5 it can be observed the variation of the emittance with the thickness for different nitrogen gas concentration. The films with both (111) and (200) crystal orientations present the lowest emittance values ( $\varepsilon = 0.17$ – $0.2$ ) and they are potential candidates for low-e applications. Table 1 shows the transmittance and emittance values against their thicknesses and

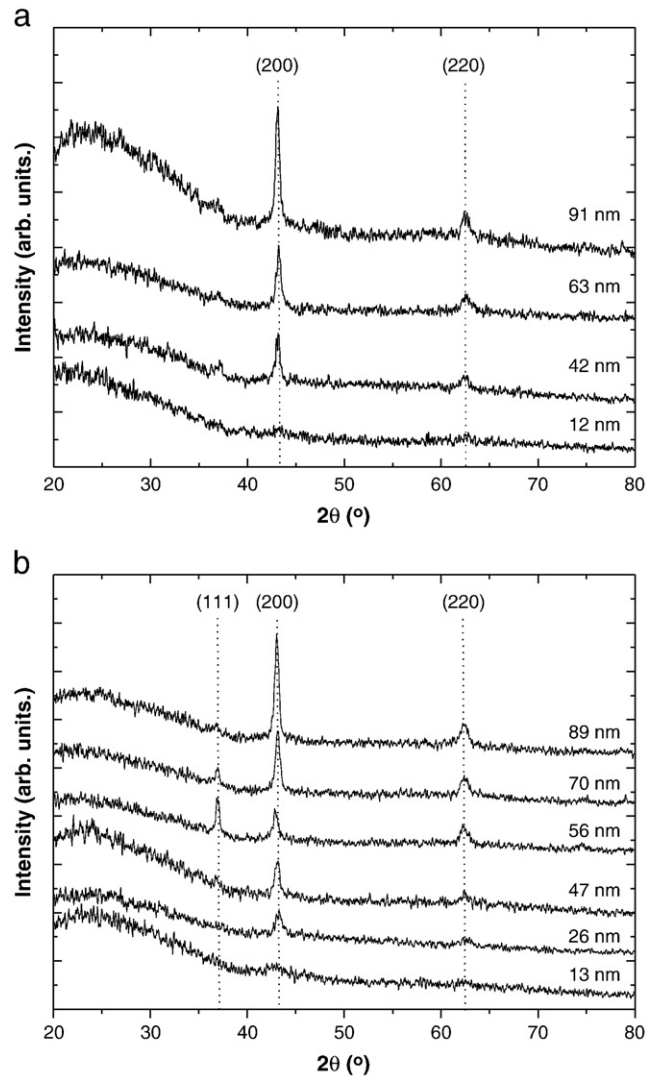


Fig. 3. XRD patterns of TiN samples for different thickness. a) Nitrogen gas concentration 30%, b) nitrogen gas concentration 40%.

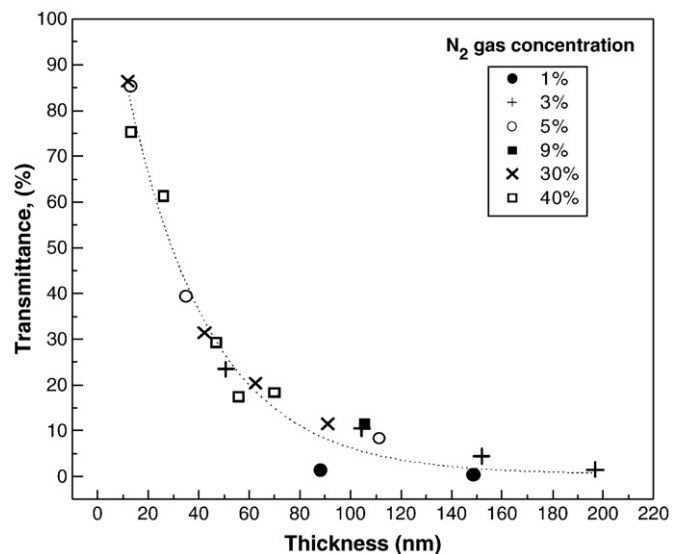


Fig. 4. Variation of the visible transmittance (measured at 600 nm) with the thickness for different nitrogen atomic contents.

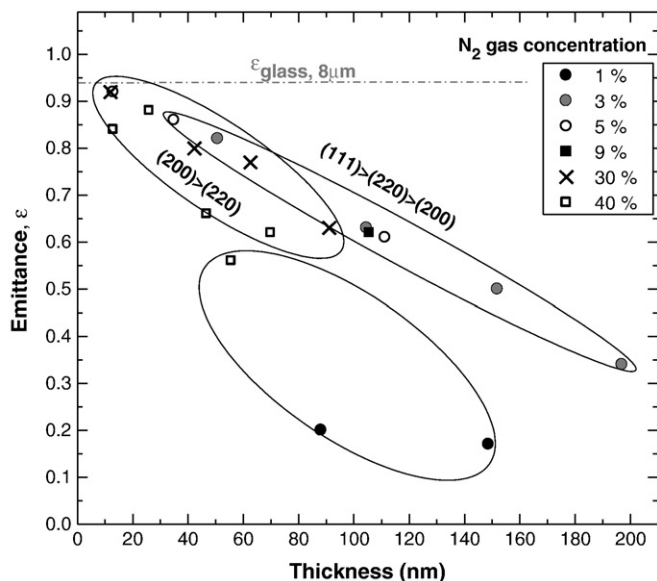


Fig. 5. Variation of the emittance, calculated at 8  $\mu\text{m}$  with the thickness for different nitrogen gas concentrations. The preferential crystal orientations are indicated.

the nitrogen gas concentration. Nevertheless, the visible transmittance should be improved in order to be employed in solar thermal collectors. Combining these low- $\epsilon$  TiN coatings with an anti-reflective layer would be a straightforward solution. On the other side, we could select TiN coating with high visible transmittance and reduce the emittance by annealing treatments as Zhao et al. [5] have recently shown.

#### 4. Conclusions

We have studied the feasibility of TiN single-layer films to be used as low- $\epsilon$  coatings. By changing the nitrogen gas concentration and the

thickness of the films, a control on the different textures can be obtained. These two parameters allow uncoupling the behaviour of the optical properties of the films, as the visible transmittance of the coatings does not depend on the preferential orientation while the emittance clearly improves with increasing the film thickness and the presence of both (111) and (200) crystal orientations. However, operational emittance values are obtained only for TiN single layers with thicknesses that severely reduce the transmittance.

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