

Reactive magnetron sputtering of Cr-N/Cr-O-N/Si-O highly selective, homogeneous and stable coating for thermal solar collectors

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Abstract

A state of the art, highly selective, homogeneous, and very stable coating deposited on aluminum foils (1m large) has been developed on an industrial continuous reactive magnetron sputtering system. A high solar absorption ($\alpha > 95\%$) and low emittance ($\epsilon < 6\%$) were achieved by carefully controlling the transition between the layers of the selective coating.

The selective coating was characterized using Visible and Near Infra Red and Fourier Transformed Infrared Red spectrometers, a thermopile emissiometer at 82.5°C (Devices & Services), and Auger Emission Spectroscopy.

After a brief description of the deposition process and system, the architecture of the selective multilayer is presented. The evolution of the reflectance measured between 360 and 2700nm, as well as α and ϵ values are presented and discussed, according to the deposition parameters of the first chromium based layers. The role of the number and nature of interfaces in the multilayer structure on the emittance of the selective coating is emphasized.

The variation of the CIE L*, a*, b* color parameters is also discussed as a function of the deposition parameters. $\Delta E < 5$ was systematically achieved on 1m large samples. In order to study the thermal stability of the selective coating, heat treatments were performed in air at 250°C for various durations. After more than 600h, nearly no change in optical properties or color are observed. Finally task X results (PC=-0.0055 after 600h) are presented.

1. Introduction

Selective surfaces with high solar absorptance between 0.3 and 2.5 μ m and low infrared (IR) emittance for wavelengths higher than 2.5 μ m are needed to provide efficient photo-thermal conversion of solar energy. Such surfaces are generally made of copper or aluminum, which provide high IR reflectance, coated with a stack of nanometric layers chosen in order to decrease the refractive index from the substrate to the coating surface and hence to improve solar absorptance [1, 2]. To further increase solar absorptance (> 0.95), an anti reflection layer (SnO₂, SiO₂, Si₃N₄, ...) is deposited on top of the absorbing stack [3]. Many selective coatings have been studied and developed so far, based on transition metal (Ti, Nb, Cr, ...) nitrides and oxynitrides. As an example, the well known titanium oxynitride coating (TiNOXTM) exhibits high absorptance (0.95) and low emittance (0.05). Recently, TiAlN/TiAlON/Si₃N₄, NbAlN/NbAlON/Si₃N₄ and Al_xO_y/Al/Al_xO_y structures [4, 5] have also been studied with absorptance higher than 0.95 and emittance in the range of 0.05-0.08. All these multilayers are deposited by means of reactive magnetron sputtering in order to achieve an excellent adhesion level, a dense morphology and a high thermal resistance. The present paper reports the reactive sputter deposition and characterization of a new Cr-N/Cr-O-N/Si-O selective coating. The role of each nanometric layer on the optical properties of the whole selective coating is studied and the

influence of the main deposition parameters on the color coordinates (CIE-Lab space) is also presented. Finally, thermal and moisture resistance tests are discussed.

2. Experimental details

Cr-N/Cr-O-N/Si-O selective coatings have been reactively sputter deposited on aluminium sheets (1m large) in an industrial continuous Physical Vapor Deposition system (BASA100-Von Ardenne). Both 'entrance' and 'exit' aluminum coils are placed under vacuum and the scrolling (i.e. deposition) speed was set to 60m/h. The ion cleaning and deposition chambers were pump down to a maximum base pressure of 5.10^{-5} mbar and backfilled with argon and the appropriate partial pressures of nitrogen and oxygen, prior deposition. The aluminum sheet was then heated to 250°C, ion cleaned thanks to an N_2/H_2 (95/5%) plasma, and deposited with Cr-N, Cr-O-N, and Si-O. The chromium based layers are deposited thanks to 3 dual magnetrons (chromium target 99.7%, 140x10 cm²) run in power regulation mode (from 7.15 to 13 W/cm²) whereas the silicon based layer is deposited thanks to 2 dual magnetrons (silicon targets 99.999%, 140x10 cm²) run in voltage regulation mode in order to avoid reactive process instability and to reach high deposition rates. All magnetrons were powered with MF power supplies. A schematic figure of the Cr-N/Cr-O-N/Si-O selective coating as well as a Auger composition profile are shown in fig. 1. The selective coating consists in two CrN layers with two compositions of nitrogen, a Cr-O-N layer and then a SiO₂ antireflection layer.

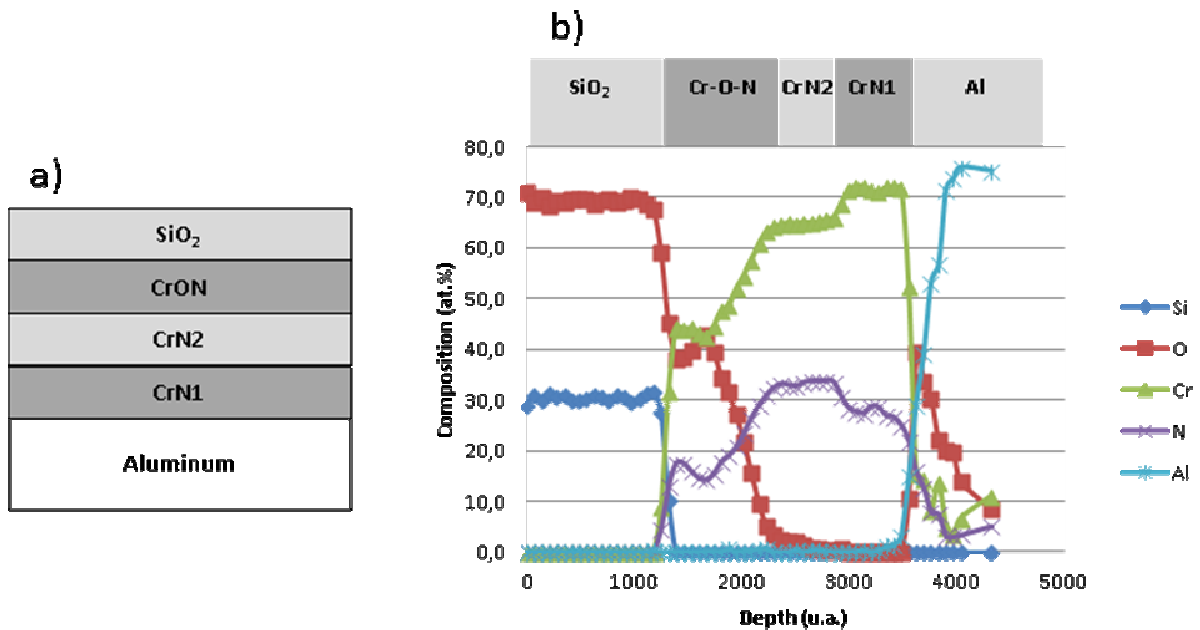


Fig. 1. Schematic figure of the Cr-N/Cr-O-N/Si-O coating a) AES composition profile b)

Total hemispherical absorptance values (α) were calculated thanks to reflexion curves acquired with a visible-near infrared spectrometer (BRUINS), with the following formula:

$$\alpha = \frac{\int_0^{\infty} (1 - r(\lambda)) \cdot S(\lambda) \cdot d\lambda}{\int_0^{\infty} S(\lambda) \cdot d\lambda} \quad (1)$$

where $C(\lambda)$ and $S(\lambda)$ are the evolutions of the reflexion of the coating as a function of the wavelength, and the solar spectrum respectively.

Total hemispherical emittance values were determined at 82°C with a M/s Devices and Services emissiometer calibrated with two standard samples with $\epsilon=0.05$ and $\epsilon=0.87$.

Concerning the color of the samples, L^* , a^* , and b^* parameters were determined thanks to the standard observer (1931-2°) and the illuminant D65.

Finally, all the samples were annealed under normal atmosphere at 250°C for various duration (up to 600h) in order to verify that the optical properties stay constant. Task X results (600h at 291°C) are also presented.

3. Results and discussion

3.1. Evolution of absorptance (α)

The multilayered selective coating was decomposed into individual layers, one bi-layer, and one tri-layer in order to determine the evolution of the reflexion as a function of the incident ray wavelength ($R\%=f(\lambda)$ curve) as shown in fig. 2, as well as the evolution of the absorptance (calculation from $R\%=f(\lambda)$ curves).

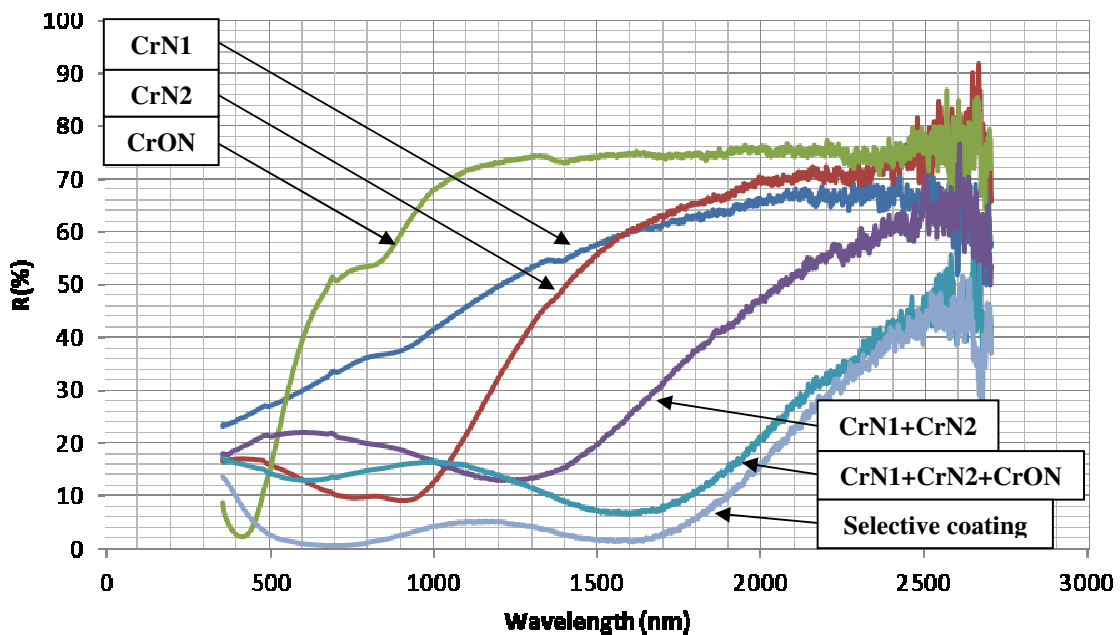


Fig. 2. Evolution of $R\%=f(\lambda)$ for the different layers, and multilayers constituting the selective coating.

Six different coatings were then deposited from the first CrN adhesive layer to the whole selective coating:

- **CrN1:** first chromium nitride coating with a low content in nitrogen. At this stage, the absorptance is not optimized ($\alpha=0.63$) as the aim of this first layer is mainly to ensure a good adhesion of the coating on the ion cleaned aluminum sheet.

- CrN2: second chromium nitride coating with a higher content in nitrogen in order to improve the absorptance ($\alpha=0.796$). The $R\%=f(\lambda)$ curve is still to 'short' (increase of $R\%$ as from 1000nm).
- CrON: chromium oxynitride layer. Alone, this layer shows a poor absorptance of 0.542, but will help to control the color of the selective coating thanks to its reflexion minimum in the visible part of the spectrum (380-780nm). The $R\%=f(\lambda)$ curve associated to this individual layer is very 'short' because this individual coating is very thin (generally the thinner the layer, the 'shorter' the $R\%=f(\lambda)$ curve).
- CrN1+CrN2: The superimposition of the two chromium nitride layers leads to an absorptance of 0.789 (similar to CrN2) but the $R\%=f(\lambda)$ curve is 'longer' because the thickness of the bi-layer is higher than the thickness of CrN2¹.
- CrN1+CrN2+CrON: Because of the further increase of the total thickness, the $R\%=f(\lambda)$ curve associated to the tri-layer has reached the optimum 'length'. Moreover a first minimum of reflexion can be seen in the visible part of the spectrum, thanks to the presence of the CrON layer. The absorptance is also increased to 0.854.
- CrN1+CrN2+CrON+SiO2: Finally, the addition of the anti reflexion SiO₂ layer increases the absorptance to a final value of **0.962** and helps to reach the blue color of the selective coating.

3.2. Evolution of emittance (ϵ)

The emittance of the previously described layers was also measured as shown in fig. 3.

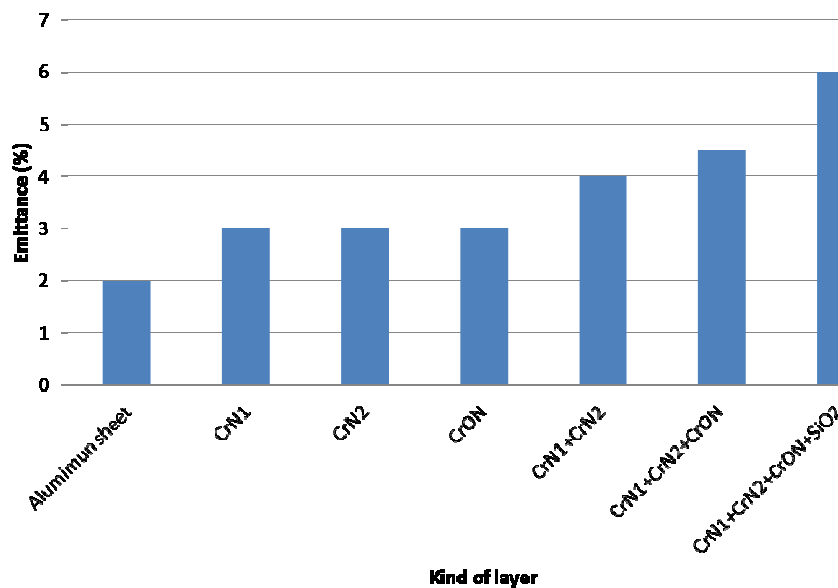


Fig. 3. Evolution of the emittance of the different layers, and multilayers constituting the selective coating.

¹ CrN2 could have been thicker to produce a 'longer' $R\%=f(\lambda)$ curve, but the adhesion of the coating would have been degraded.

As expected the aluminum sheet presents the lowest IR emittance of 0.02, whereas CrN1, CrN2 and CrON are characterized by similar emittances of 0.03. Then, the emittance gradually increases when the different layers are stacked, to reach 0.06 for the final selective coating.

Thus, the emittance seems to be proportional to the number of interfaces between layers as shown in fig. 4. This behavior makes sense as each interface is the place of multi-reflexion phenomena which directly affect the total emittance of the coating. Generally, the rougher the interfaces the higher the increase of the total emittance. As shown in fig.1 (AES profile) the interfaces of our selective coating are well defined because sputtering chambers are physically separated. However, as CrN2 and CrON are deposited in the same chamber, the interface between these two layer is smoother, which explains that the emittance of the CrN1+CrN2+CrON stack is only 0.045.

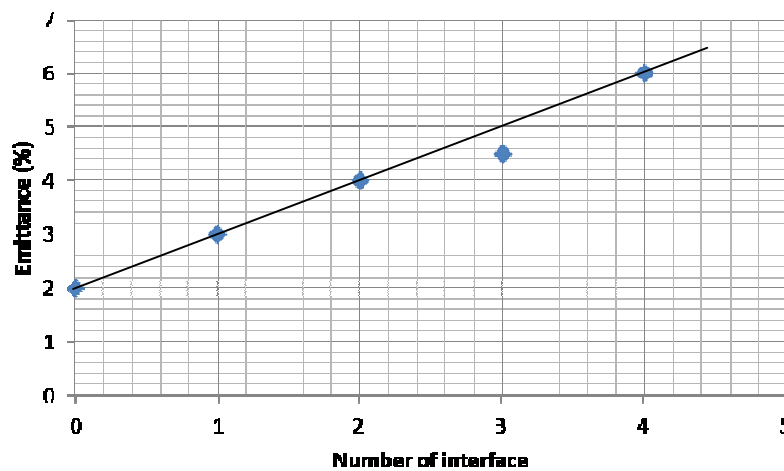


Fig. 4. Evolution of the emittance as a function of the number of interfaces of the multilayered selective coating.

According to M. Farooq et al [6], thermal emittance is affected first by the quality (i.e. density, porosity, roughness) and then by the total thickness of nickel plated copper. Even if the deposition technique is not the same, this is in good agreement with our result where each interface can be considered as a defect zone between homogeneous layers.

3.3. Color parameters

In order to obtain a blue/violet color with L^* , a^* , b^* parameters as close as possible to 20 to 25, 7 ± 1 , and -27 ± 1 respectively, the influence of the main deposition parameters on the shape of the $R\% = f(\lambda)$ was studied. Basically, the deposition rate (i.e. thickness) and the composition of the layers were modified.

Fig. 5 presents schematically the evolution of the shape of the $R\% = f(\lambda)$ curve (360 to 2700nm) and hence the evolution of the color parameters when:

- The power is increased on the chromium targets
- The deposition rate of SiO_2 is increased
- The oxygen flow rate is decreased on the chromium target used to synthesize CrON
- The nitrogen flow rate is decreased on the chromium target used to synthesize CrON

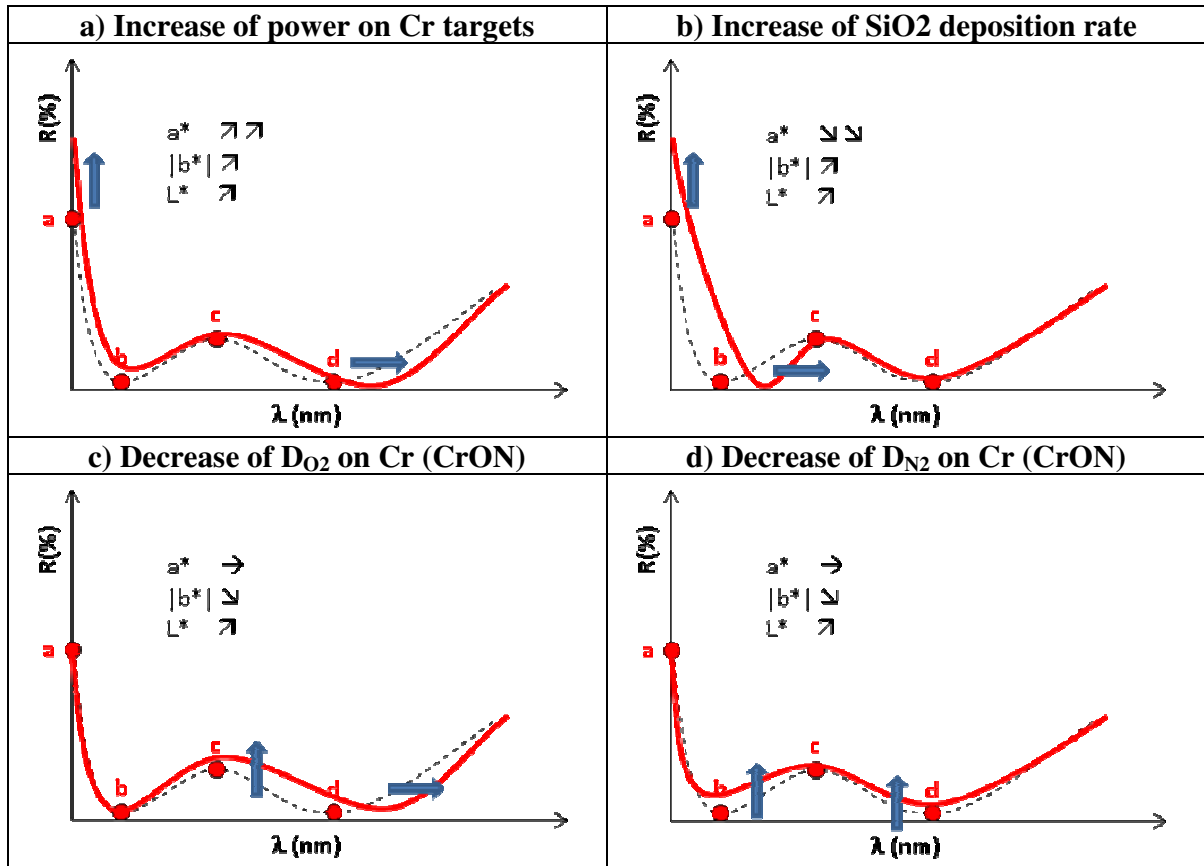


Fig. 5. Influence of the main deposition parameters on the evolution of the shape of the $R\%=f(\lambda)$ curve (i.e. color parameters).

As we can see on fig. 5. a^* (green to red axis) is very sensitive to the thickness of CrON and SiO₂ layers and can not be adjusted without a slight modification of b^* (blue to yellow axis). On the other hand, the modification of the composition of CrON enables to adjust slightly adjust b^* , a^* remaining constant. Finally, the increase of R% in the range of 360-780nm always leads to an increase of L (black to white axis).

In order to guaranty an homogeneous color on the whole width of the aluminum sheet (1m) all reactive gases are distributed along the dual magnetrons. As the color parameters are particularly sensitive to the Si-O deposition, optical fibers continuously monitor the evolution of the silicon sputter flux on both edges and in the middle of the targets. This ensures the deposition of an homogeneous selective coating, as shown in fig. 6 where $R\%=f(\lambda)$ curves of 9 samples taken from an edge to other one of the coated aluminum sheet.

For this particular set of samples the absorptance varied between 0.955 and 0.962 (difference less than 1%), the emittance was constant and equal to 0.06, and the color parameters were $L^*=20$, $a^*=8$ and $b^*=-28$.

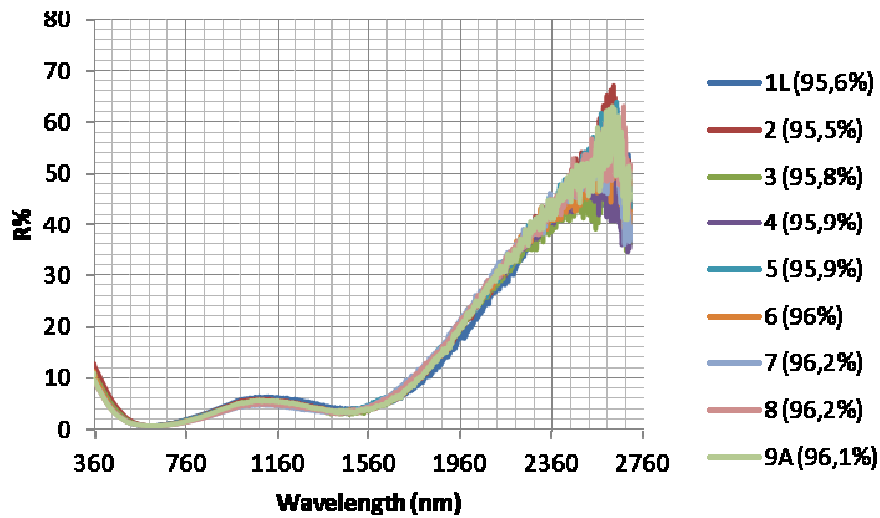


Fig. 6. $R\%=f(\lambda)$ curves of 9 samples taken from an edge to other one of the coated aluminum sheet.

3.4. Thermal stability and task X results

In order to verify that the coating will be stable in real conditions of use selective coatings were annealed in air at 250°C during 300h. Fig. 7. presents $R\%=f(\lambda)$ curves obtained before and after annealing.

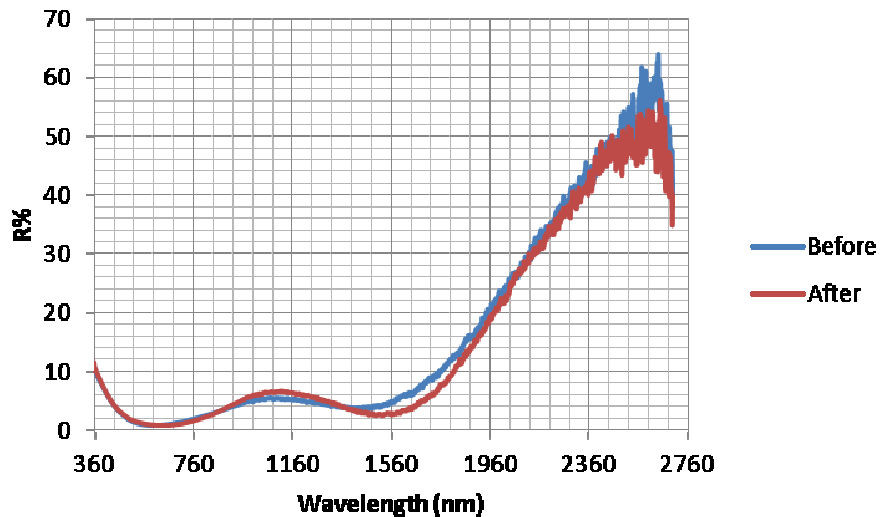


Fig. 7. $R\%=f(\lambda)$ curves obtained before and after annealing at 250°C during 300h.

After annealing, the color of the selective coating remains exactly the same as no modification of the $R\%=f(\lambda)$ curve has been observed between 360 and 780nm (visible spectrum). For higher wavelengths a slight evolution of the $R\%=f(\lambda)$ curve has been reported which probably correspond to the reorganization of atoms (diffusion mechanism), mainly at the layer interfaces, and hence to local

change of composition. This assumption seems to be confirmed by the fact that the emittance is slightly better after annealing. Task X results confirm this behavior as discussed in the following.

Fig 8. presents a figure caption of the task X report concerning thermal stability tests performed on our selective coating.

Table 2: Results for the optical properties and the performance criterion $PC = \Delta\alpha - 0.5 \Delta\epsilon$ at testing temperature $T1 = 291^\circ\text{C}$						
Total testing time /h	0	36	75	150	300	600
Solar Absorptance (AM1.5):	0,953	0,957	0,957	0,957	0,956	0,954
Thermal Emittance (100°C):	0,053	0,061	0,060	0,071	0,048	0,044
Performance $\Delta P = \Delta\alpha - 0,5 \Delta\epsilon$:	0	0	0	0,0050	-0,0050	-0,0055

Fig. 8. Task X report concerning thermal stability tests.

As we can see, the absorptance remains constant whatever the test duration at 291°C , whereas the thermal emittance decreases from 0.053 to 0.044. As said previously this behavior should be due to a less rough transition between the various layers of the selective coating, due to nitrogen and oxygen diffusion at the interfaces. Thus, a performance criterion of -0.0055 was achieved. After 600h at 291°C the adhesion of the selective coating was still excellent.

Concerning the condensation (moisture) tests, the optical properties of the selective coating remain constant, leading to a performance criterion equal to 0. After 600h at 40°C in humid atmosphere the adhesion of the selective coating was still excellent.

4. Conclusion

In this paper the deposition parameters and the optical properties of a new CrN/CrON/SiO_2 selective coating for solar thermal applications were presented and discussed. It was shown that a precise control of the deposition parameters are needed to ensure a good solar absorptance with an homogeneous blue/violet color of the coating. Solar absorptance and thermal emittance of 0.957 and 0.053 were reported according to task X results. The initial value of emittance of 0.053 (0.02 for pure aluminum) is due to rough transition between the layers of selective coatings. After annealing the emittance is reduced to 0.044 certainly thanks to diffusion of nitrogen and oxygen at the interfaces.

References

- [1] G. Hass, M.H. Francombe, Physics of Thin Films, Vol. 10, Academic press, New York, 1978.
- [2] M. Adsten, R. Joerger, K. Jarrendahl, E. Wackelgard, Sol. Energy, 68 (2000) 325.
- [3] I.T. Ritchie, B. Window, Appl. Opt., 16 (1977) 1438.
- [4] H.C. Barshilia, N. Selvakumar, K.S. Rajam, A. Biswas, Solar Energy Materials & Solar Cells, 92 (2008) 495.
- [5] H.C. Barshilia, N. Selvakumar, G. Vignesh, K.S. Rajam, A. Biswas, Solar Energy Materials & Solar Cells, 93 (2009) 315.
- [6] M. Farooq, I. A. Raja, Renewable Energy, 33 (2008) 1275.