

Preparation and Optimization of NbCrN/NbCrON/SiO₂ Solar Selective Absorbing Coating

Beibei Dai¹, Cong Wang^{1,*}, Ying Sun¹, Lei Wang¹, Yuping Ning¹, Ping Song¹, Yilin Zhang¹, Yongxin Wu¹, Eric Tomasella² and Angélique Bousquet²

¹Center for Condensed Matter and Material Physics, Department of Physics, Beihang University, Beijing 100191, China

²Université Clermont Auvergne, CNRS, Institut de Chimie de Clermont-Ferrand (ICCF), F-63000 Clermont-Ferrand, France

Abstract: A novel Cu/NbCrN/NbCrON/SiO₂ solar selective absorbing coating was successfully prepared by magnetron sputtering. In this coating, Cu, NbCrN, NbCrON and SiO₂ act as the infrared reflector metal layer (and as substrate too), high metal volume fraction layer, low metal volume fraction layer and anti-reflection layer, respectively. The effects of the reactive gas flow rates of the absorption layers and the thickness of each layer were investigated and the optimal deposition parameters for the coatings were obtained. Finally the main result is that the best spectral properties with the absorptance of 0.93 and the emittance of 0.07 (25°C) are achieved. The experimental results indicate its potential applications in solar collectors.

Keywords: NbCrON, solar selective absorbing coating, magnetron sputtering, spectral selectivity.

1. INTRODUCTION

Solar thermal utilization is one of the important fields in solar energy applications. One of the important component sinsolar photothermal applications is solar collector, which uses solar selective absorbing coating (SSAC) as the critical photo-thermal conversion surface [1-5]. An ideal solar selective absorbing coating should have a highest solar absorptance α (close to one) in solar radiation range (300–2500 nm) and a lowest thermal emittance ε (close to zero) in infrared (IR) range (>2500 nm) [6]. According to the typical double interference structure [7], a SSAC consists of an IR-reflective metallic layer, a high metal volume fraction (HMFV) cermet absorption layer, a low metal volume fraction (LMVF) cermet absorption layer and an anti-reflection ceramic layer from bottom to top [8-10].

Recently, the SSACs based on transition metal nitrides and oxynitrides, have been reported due to their outstanding spectral selectivity, excellent oxidation resistance, and excellent chemical inertness [11-13], such as TiAlN/TiAlON/Si₃N₄ [6,14], NbAlN/NbAlON/Si₃N₄ [15], Ti_{0.5}Al_{0.5}N/Ti_{0.25}Al_{0.75}N/AlN [13], HfMoN/HfON/Al₂O₃ [16,17] and CrMoN/CrON [18]. In our previous work, we have reported the Nb-NbN [19], NbTiON(M)/NbTiON(D)/SiON [8] and NbMoN/NbMoON/SiO₂ [9] coatings, which indicated that niobium based nitrides had good spectral selectivity and thermal

stability. It was reported recently that the chromium based nitrides such as CrN_xO_y/SiO₂ [20], Cr_xO_y/Cr/Cr₂O₃ [21] and AlCrSiN/AlCrSiON/AlCrO [22] are being developed for solar thermal applications. However, there was no report about niobium chromium nitride/oxynitride as solar selective absorbing coating. Therefore, we develop a new solar selective absorbing coating Cu/NbCrN/NbCrON/SiO₂, which uses NbCrN/NbCrON bilayer as the absorption layer, so as to obtain an excellent spectral selectivity.

In this article, the Cu/NbCrN/NbCrON/SiO₂ coating was prepared by magnetron sputtering and its optical properties are discussed. The effects of the reactive gas flow rates for preparing the absorption layers and the thickness of each layer on the spectral properties were investigated and the optimal deposition parameters for the coatings were obtained.

2. EXPERIMENTS

The NbCrN, NbCrON and SiO₂ layers were deposited by a magnetron sputtering system with multi-target arrangement (JGP350C). The base pressure was lower than 1×10⁻⁴Pa. A pre-sputtering procedure was carried out to clean the target surface in the vacuum chamber under Ar atmosphere for 30 min. The Ar flow was kept constant at 50 sccm in the deposition process of each layer. A Cr target (Φ60 mm×3 mm, 99.95% purity) with Nb slices (10 mm×10 mm×1 mm, 99.99% purity) on it was used to deposit the NbCrN and NbCrON layers in an Ar + N₂ and Ar + N₂ + O₂atmosphere, respectively. The details are presented

*Address correspondence to this author at the Center for Condensed Matter and Material Physics, Department of Physics, Beihang University, Beijing 100191, China; Tel:+86 10 82338346; E-mail: congwang@buaa.edu.cn

Table 2: Deposition Parameters for Individual Layers of the Cu/NbCrN/NbCrON /SiO₂ Coating

Layer	Sputtering Method	Substrate-to-Target Distance(mm)	Sputtering Pressure (Pa)	Power Density (W/cm ²)
NbCrN	DC	60	1.0	4.23
NbCrON	DC	60	1.0	4.60
SiO ₂	RF	80	0.5	3.54

in Table 1. The SiO₂ layer was prepared by sputtering aSi target (Φ60 mm×3 mm, 99.99% purity) under an Ar/O₂ (8 sccm) atmosphere. The individual layers and multilayer coatings were deposited on copper (Cu)substrate (30 mm×30 mm ×0.1 mm). All substrates were cleaned using alcohol followed by de-ionized water in an ultrasonic agitator before being deposited. The deposition parameters of each layer are listed in Table 2.

Table 1: Reactive Gas Flow Rates of the NbCrN and NbCrON Layers

Nitride Samples	N ₂ flowrate (sccm)	Oxynitride Samples	N ₂ Flow Rate (sccm)	O ₂ Flow Rate (sccm)
S1	9	S6	21	1
S2	12	S7	21	2
S3	15	S8	21	3
S4	18	S9	21	4
S5	21	S10	21	5

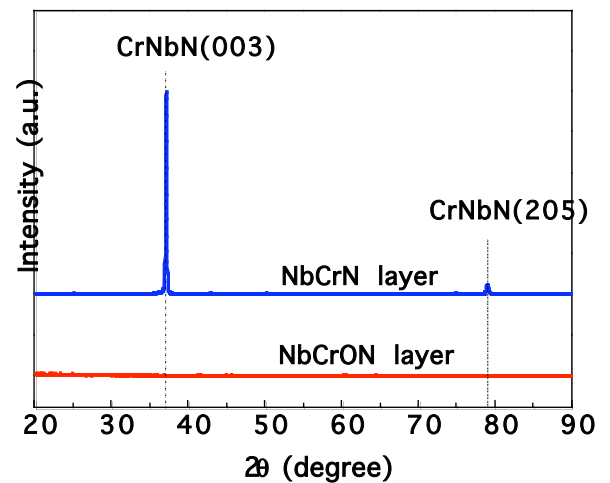
The crystal structure of the NbCrN and NbCrON layers was investigated by x-ray diffraction. Dektak 6 M surface profiler was used to measure the thickness of each layer. The 900UV/VIS/NIR equipped with an integrating sphere coated with barium sulphate was used to measure the reflectance (R) spectra in the wavelength range of 0.3-1.7 μm. The Bruker Tensor 27 is a type of Fourier Transform Infrared Reflectance (FTIR) spectrometer equipped with an integrating sphere coated with gold which was used to measure the thermal emittance of the coating [20]. The solar absorptance is calculated by Eqs. (1) and (2) [23, 24], where $I_s(\lambda)$ and $I_b(\lambda, T)$ are the solar spectrum and the blackbody radiation spectrum at temperature T, respectively.

$$\alpha = \frac{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} (1 - R(\lambda)) I_s(\lambda) d\lambda}{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} I_s(\lambda) d\lambda} \quad (1)$$

$$\varepsilon_T = \frac{\int_{2.5\mu\text{m}}^{25\mu\text{m}} (1 - R(\lambda)) I_b(\lambda, T) d\lambda}{\int_{2.5\mu\text{m}}^{25\mu\text{m}} I_b(\lambda, T) d\lambda} \quad (2)$$

3. RESULTS AND DISCUSSION

To analyze the crystal structure of NbCrN (S5) and NbCrON (S7) layers, NbCrN (S5) and NbCrON (S7) layers were deposited on glass substrates, respectively. And the thickness of each layer is about 1000 nm. Figure 1 shows the x-ray diffraction patterns of the NbCrN (S5) and NbCrON (S7) layers. The XRD data of the nitride layer shows a high-intensity diffraction peak at $2\theta = 36.727^\circ$ which corresponds to CrNbN (003), and a low-intensity diffraction peak at $2\theta = 78.843^\circ$ which corresponds to CrNbN (205), respectively. The XRD pattern of the oxynitride layer does not exhibit any XRD peaks, which means it is an amorphous phase.

**Figure 1:** XRD patterns of the NbCrN and NbCrON layers deposited on glass substrates.

The structure schematic of the coating is illustrated in Figure 2 [25]. It is worthwhile to mention that the optical properties of the coating are very sensitive to any changes in the reactive gas flow rates and

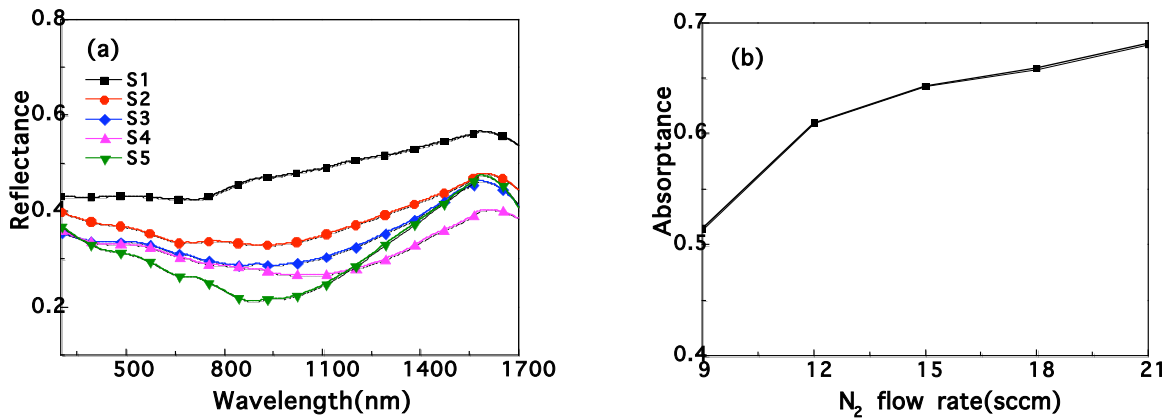


Figure 3: Reflectance spectra (a) and absorbance values (b) of the NbCrN layers (thickness: 40 nm) deposited on Cu substrate with different nitrogen gas flow rates.

thickness of each layer [9, 26]. Therefore, a number of experimental scenarios have been designed and performed systematically in order to optimize the coating.

3.1. Optimization of The NbCrN Layer

Figure 3(a) shows the R spectra of the NbCrN layers deposited on Cu substrate with different nitrogen flow rates in the wavelength range of 300 – 1700 nm, and the thicknesses of the NbCrN layers are fixed at 40 nm. The R spectra decrease with nitrogen flow rate, resulting in the absorbance increasing with nitrogen flow rate as shown in Figure 3(b). However, when the nitrogen flow rate is above 21 sccm, the Cr target is poisoned in the reactive sputtering mode. That's why the highest value of nitrogen flow rate is 21 sccm and is considered as the optimum nitrogen flow rate for preparing the NbCrN layer. The absorbance has the highest value with this deposition condition.

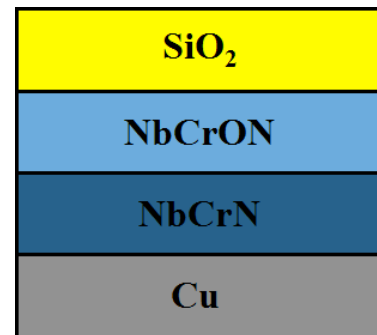


Figure 2: Schematic of the Cu/NbCrN/ NbCrON /SiO₂ coating.

The R spectra in the wavelength range of 300–1700 nm of the NbCrN layers deposited on Cu substrate by changing the layer thickness from 20 nm to 60 nm are shown in Figure 4(a), and the nitrogen flow rate of the NbCrN layer is fixed at 21 sccm as said before. The R spectra in the wavelength range of 500 - 1100 nm increase with the NbCrN layer thickness, and decrease

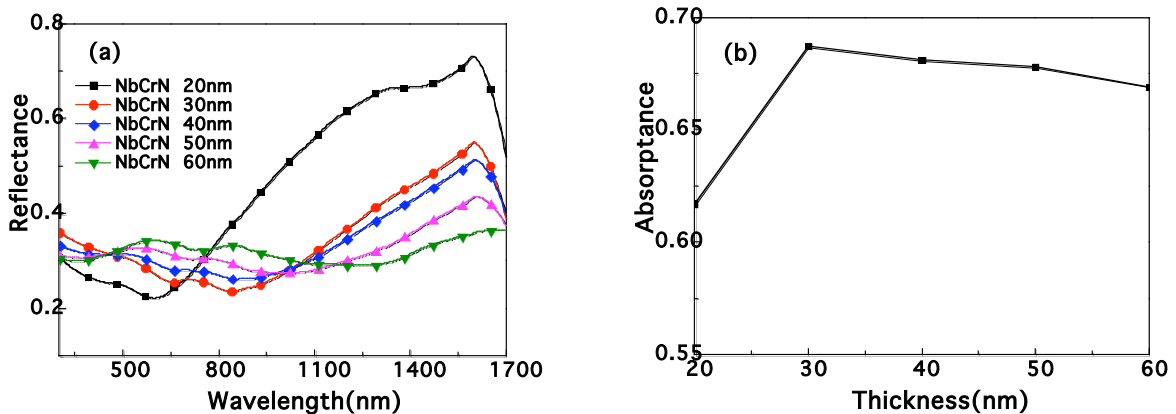


Figure 4: Reflectance spectra (a) and absorbance values (b) of the NbCrN layers deposited on Cu substrate with different NbCrN layer thicknesses.

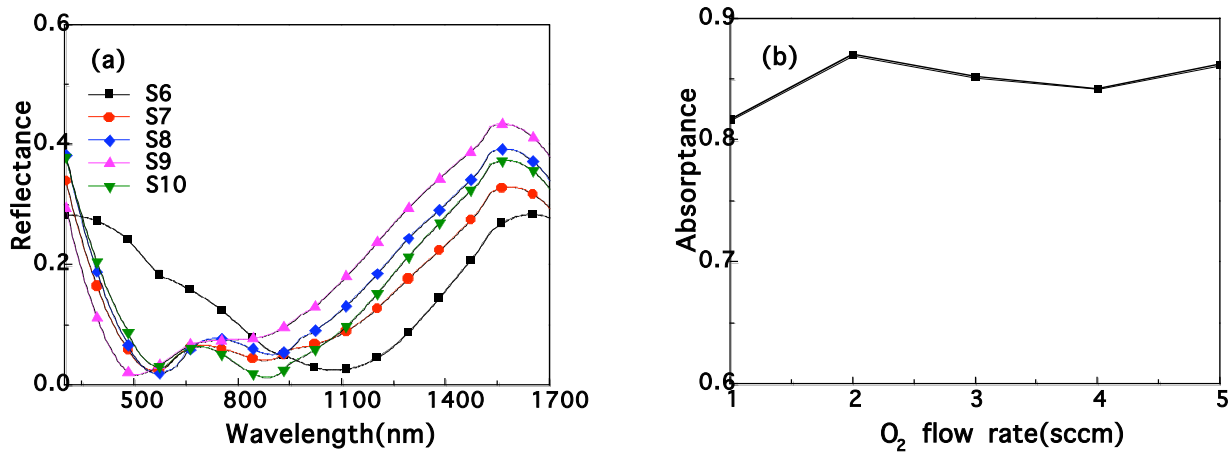


Figure 5: Reflectance spectra (a) and absorbance values (b) of the Cu/NbCrN/NbCrON layers with different oxygen gas flow rates for preparing NbCrON layer.

with thickness increasing in the wavelength above 1100 nm. As Figure 4(b) shows, the absorbance first increases and then slightly decreases. The NbCrN layer achieves the highest absorbance when the layer thickness is 30 nm, which is chosen as the optimal thickness for the NbCrN layer in the next optimization process.

3.2. Optimization of The NbCrON Layer

Figure 5(a) shows the R spectra of the Cu/NbCrN/NbCrON by only changing the oxygen flow rates for LMVF layer in the wavelength range of 300–1700 nm. The nitrogen flow rate for both NbCrN and NbCrON layers is fixed at 21 sccm, and the thicknesses of NbCrN and NbCrON layers are 30 nm and 50 nm, respectively. It can be observed that when the oxygen flow rate increases, the R spectrain the wavelength range of 1100 - 1700 nm initially increases,

reaches a maximum for S9 and then decreases. The S6 doesn't have an interference peak near 700 nm compared with other samples. This is the reason that the oxygen flow rate for S6 is too low to distinguish the optical properties of the S5 and S6 samples. The absorbance values as a function of oxygen flow rate for the LMVF layer are shown in Figure 5(b). With increasing the oxygen flow rate from 1.0 to 2.0 sccm, the absorbance increases; whereas above 2 sccm, no more obvious change is observed. Thus the oxygen flow rate of 2 sccm for the NbCrON layer is chosen.

The R spectra in the wavelength range of 300–1700 nm of the Cu/NbCrN/ NbCrON with different LMVF layer thickness (from 40 nm to 80 nm) are shown in Figure 6(a). From previous optimization, the nitrogen flow rate for the NbCrN and NbCrON layers is 21 sccm, the oxygen flow rate for the NbCrON layer is 2 sccm and the thickness of NbCrN layer is 30 nm. The R

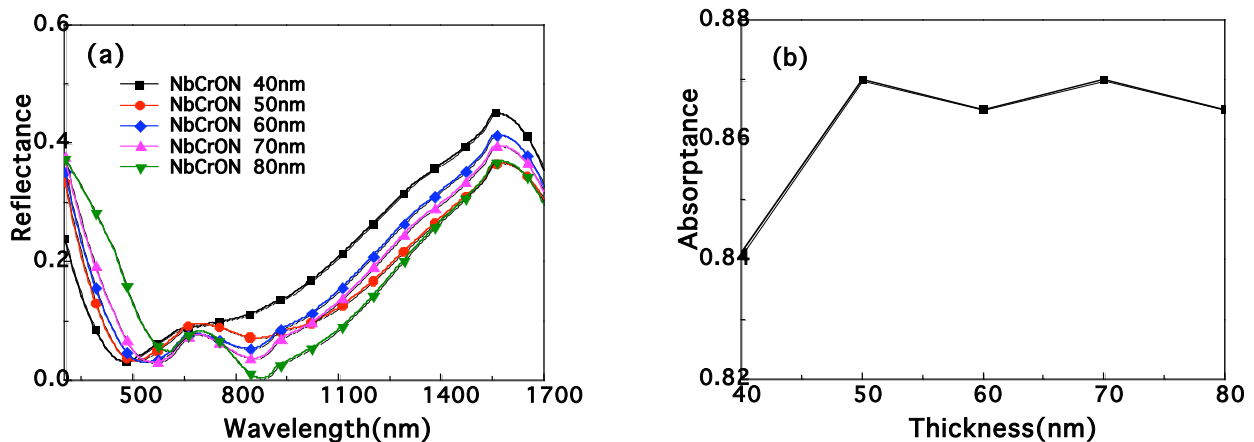


Figure 6: Reflectance spectra (a) and absorbance values (b) of the Cu/NbCrN/NbCrON layers with different NbCrON layer thicknesses.

spectra has a red shift as the NbCrON layer thickness increases, which results in the R spectra increasing with the NbCrON layer thickness in the wavelength range of 300-500nm. This will lead to the decrease of the absorptance, which is not our expectation. The intensity of interference peak decreases with the NbCrON layer thickness in the wavelength region of 500-950nm, which causes the increase of the absorptance. As shown in Figure 6(b), the absorptance has no significant change when the thickness is above 50nm. The highest absorptance value is obtained when the NbCrON layer thickness is 50nm, which is chosen as the optimal thickness for the NbCrON layer in the next optimization process.

3.3. Optimization of The SiO₂ Layer

Figure 7(a) shows the R spectra of the Cu/NbCrN/NbCrON/SiO₂ coating with different SiO₂ layer thickness from 70–110nm, and the thicknesses of NbCrN and NbCrON layers are 30nm and 50nm, respectively. S5 and S6 are taken as the absorption layers. As Figure 7(a) shows, the R spectra has a red shift as the SiO₂ layer thickness increases, and the interference peak intensity is weakened in the wavelength range from 400-700 nm. This impairs the absorptance in the wavelength range from 300–500 nm whereas it enhances the absorptance in the wavelength range from 400-700 nm, respectively. The R spectra increase with the SiO₂ layer thickness in the wavelength region from 600-1700nm which decreases the absorptance.

The solar absorptance values as a function of the SiO₂ layer thickness are shown in Figure 7(b). With increasing of the thickness, the absorptance value first increases and then decreases. This is due to the

mutual balance competition between the red shift of the R spectra which decreases the absorptance and the weakened intensity of the interference peak which enhances the absorptance. For comprehensive consideration of the high absorptance for the coating, we choose 80 nm as the optimum thickness of the SiO₂ layer.

The reflectance spectra of layer-added optimal tandem absorber in solar spectrum range are presented in Figure 8. The optimized Cu/NbCrN/NbCrON/SiO₂ coating exhibits the low reflectance in 300-2500 nm region and high reflectance in the wavelength range of 2.5-25 μm. The reflectance curve rises sharply from 2000 nm. The measured solar absorptance of the coating is 0.93 and emittance is 0.07 (25°C). According to our primary experiments, this tandem absorber is believed to have excellent thermal stability, which will be reported in another article.

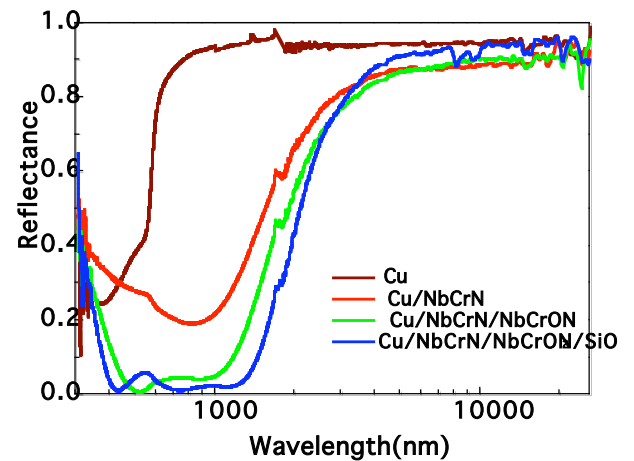
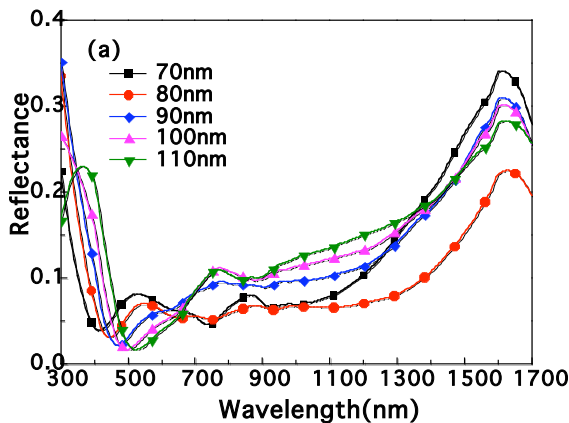


Figure 8: Reflectance spectra of layer-added optimal tandem absorber in solar spectrum range.

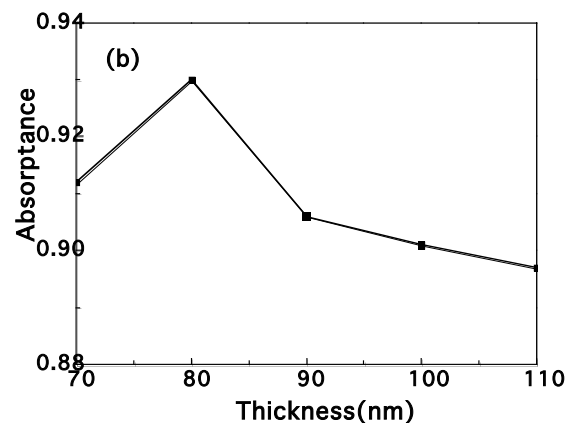


Figure 7: Reflectance spectra (a) and absorptance values (b) of the Cu/NbCrN/NbCrON/ SiO₂ layers with different SiO₂ layer thicknesses.

CONCLUSION

A novel solar selective absorbing coating of Cu/NbCrN/NbCrON/SiO₂ with a high absorptance of 0.93 and low emittance of 0.07 (25 °C) was prepared using magnetron sputtering. Through adjusting and optimizing the nitrogen and oxygen flow rates, and thickness of each layer, the optimal deposition parameters for the coatings are obtained. The optimal nitrogen and oxygen flow rates of the NbCrN and NbCrON coatings are 21sccm and 2sccm, respectively. The optimum thicknesses of the NbCrN, NbCrON and SiO₂ layers are 30 nm, 50 nm and 80 nm, respectively. The coating possesses excellent spectral selectivity and has a potential application for solar collector.

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REFERENCES

- [1] Selvakumar N nad Barshilia HC. Review of physical vapor deposited (PVD) spectrally selective coatings for mid- and high-temperature solar thermal applications. *J Solar Energy Materials and Solar Cells* 2012; 98(5):1-23. <https://dx.doi.org/10.1016/j.solmat.2011.10.028>
- [2] Kennedy CE. Review of mid-to high-temperature solar selective absorber materials. R. No. NREL/TP-520-31267. Golden: National Renewable Energy Laboratory of US, 2002.
- [3] Xue YF, Wang C, Wang WW, Liu Y, Wu YX, Ning YP, et al. Spectral properties and thermal stability of solar selective absorbing AlNi–Al₂O₃ cermet coating. *J Solar Energy* 2013; 96:113-118. <https://dx.doi.org/10.1016/j.solener.2013.07.012>
- [4] Wang J, Wei BC, Wei QR and Li DJ. Optical property and thermal stability of Mo/ Mo–SiO₂/SiO₂ solar-selective coating prepared by magnetron sputtering. *J Physica Status Solidi (A)* 2011; 208 (3): 664-667. <https://dx.doi.org/10.1002/pssa.201026301>
- [5] Zhang QC, Yin Y and Mills DR. High efficiency Mo □ Al₂O₃ cermet selective surfaces for high-temperature application[J]. *Solar Energy Materials and Solar Cells* 1996; 40(1): 43-53. [https://dx.doi.org/10.1016/0927-0248\(95\)00078-X](https://dx.doi.org/10.1016/0927-0248(95)00078-X)
- [6] Barshilia HC, Selvakumar N, Rajam KS, SridharaRao DV, Muraleedharan K, et al. TiAlN/TiAlON/Si₃N₄ tandem absorber for high temperature solar selective applications. *J Applied Physics Letters* 2006; 89(19): 191909. <http://dx.doi.org/10.1063/1.2387897>
- [7] Zhang QC and Mills DR. Very low - emittance solar selective surfaces using new film structures. *J Journal of Applied Physics* 1992; 72(7):3 013-3021. <http://dx.doi.org/10.1063/1.351510>
- [8] Liu Y, Wang C and Xue Y. The spectral properties and thermal stability of NbTiON solar selective absorbing coating. *J Solar Energy Materials and Solar Cells* 2012; 96(1): 131-136. <https://dx.doi.org/10.1016/j.solmat.2011.09.034>
- [9] Wu YX, Wang C, Sun Y, Xue YF, Ning YP, Wang WW, et al. Optical simulation and experimental optimization of Al/NbMoN/NbMoON/SiO₂ solar selective absorbing coatings. *J Solar Energy Materials and Solar Cells* 2015; 134: 373-380. <http://dx.doi.org/10.1016/j.solmat.2014.12.005>
- [10] Ning YP, Wang WW, Wang L, Sun Y, Song P, Man HL, et al. Optical simulation and preparation of novel Mo/ZrSiN/ZrSiON/SiO₂ solar selective absorbing coating. *J Solar Energy Materials and Solar Cells* 2017; 167: 178-183. <http://dx.doi.org/10.1016/j.solmat.2017.04.017>
- [11] Rebouta L, Pitães A, Andritschky M, Capela P, Cerqueira MF, Matilainen A, et al. Optical characterization of TiAlN/TiAlON/SiO₂ absorber for solar selective applications. *J Surface and Coatings Technology* 2012; 211(42): 41-44. <https://dx.doi.org/10.1016/j.surfcoat.2011.09.003>
- [12] Wu YX, Wang C, Sun Y, Ning YP, Liu YF, Xue YF, et al. Study on the thermal stability of Al/NbTiSiN/NbTiSiON/SiO₂ solar selective absorbing coating. *J Solar Energy* 2015; 119: 18-28. <https://dx.doi.org/10.1016/j.solener.2015.06.021>
- [13] Du M, Liu XP, Hao L, Wang XJ, Mi J, Jiang LJ, et al. Microstructure and thermal stability of Al/Ti_{0.5}Al_{0.5}N/Ti_{0.25}Al_{0.75}N/AlN solar selective coating. *J Solar Energy Materials and Solar Cells* 2013; 111(4): 49-56. <https://dx.doi.org/10.1016/j.solmat.2012.12.010>
- [14] Barshilia HC, Selvakumar N, Rajam KS, SridharaRao DV and Muraleedharan K. Deposition and characterization of TiAlN/TiAlON/Si₃N₄ tandem absorbers prepared using reactive direct current magnetron sputtering[J]. *Thin Solid Films* 2008; 516(18): 6071-6078. <https://dx.doi.org/10.1016/j.tsf.2007.10.113>
- [15] Barshilia HC, Selvakumar N, Rajam KS and Biswas A. Spectrally selective NbAlN/ NbAlON/Si₃N₄ tandem absorber for high-temperature solar applications. *J Solar Energy Materials and Solar Cells* 2008; 92(4): 495-504. <https://dx.doi.org/10.1016/j.solmat.2007.11.004>
- [16] Selvakumar N, Manikandanath NT, Biswas A and Barshilia HC. Design and fabrication of highly thermally stable HfMoN/HfON/Al₂O₃ tandem absorber for solar thermal power generation applications. *J Solar Energy Materials and Solar Cells* 2012; 102(4): 86-92. <https://dx.doi.org/10.1016/j.solmat.2012.03.021>
- [17] Selvakumar N, Prajith K, Biswas A and Barshilia HC. Optical simulation and fabrication of HfMoN/HfON/Al₂O₃ spectrally selective coating. *J Solar Energy Materials and Solar Cells* 2015; 140: 328-334. <https://dx.doi.org/10.1016/j.solmat.2015.04.031>
- [18] Selvakumar N, Santhoshkumar S, Basu S, Biswas A and Barshilia HC. Spectrally selective CrMoN/CrON tandem absorber for mid-temperature solar thermal applications. *J Solar Energy Materials and Solar Cells* 2013; 109(5): 97-103. <https://dx.doi.org/10.1016/j.solmat.2012.10.003>
- [19] Du XK, Wang TM, Wang C, Chen BL and Zhou L. Microstructure and optical characterization of magnetron sputtered NbN thin films. *J Chinese Journal of Aeronautics* 2007; 20(2): 140-144. [https://dx.doi.org/10.1016/S1000-9361\(07\)60021-1](https://dx.doi.org/10.1016/S1000-9361(07)60021-1)
- [20] Wu L, Gao JH, Liu ZM, Liang LY, Xia F and Cao HT. Thermal aging characteristics of CrN_xO_y solar selective absorber coating for flat plate solar thermal collector applications. *J Solar Energy Materials and Solar Cells* 2013; 114(114): 186-191. <https://dx.doi.org/10.1016/j.solmat.2013.03.005>
- [21] Barshilia HC, Selvakumar N, Rajam KS and Biswas A. Structure and optical properties of pulsed sputter deposited Cr_xO_y/Cr/Cr₂O₃ solar selective coatings. *J Journal of Applied*

- Physics 2008; 103(2): 023507.
<http://dx.doi.org/10.1063/1.2831364>
- [22] Zou CW, Xie W and Shao LX. Functional multi-layer solar spectral selective absorbing coatings of AlCrSiN/AlCrSiON/AlCrO for high temperature applications. J Solar Energy Materials and Solar Cells 2016; 153: 9-17.
<https://dx.doi.org/10.1016/j.solmat.2016.04.007>
- [23] Liu HD, Wan Q, Xu YR, Luo C, Chen YM, Fu DJ, *et al.* Long-term thermal stability of CrAlO-based solar selective absorbing coating in elevated temperature air. J Solar Energy Materials and Solar Cells 2015; 134: 261-267.
<https://dx.doi.org/10.1016/j.solmat.2014.12.009>
- [24] Wang XL, Wu XF, Yuan L, Zhou CP, Wang YX, Huang KK, *et al.* Solar selective absorbers with foamed nanostructure prepared by hydrothermal method on stainless steel. J Solar Energy Materials and Solar Cells 2016; 146: 99-106.
<https://dx.doi.org/10.1016/j.solmat.2015.11.040>
- [25] Zhang QC and Mills DR. New cermet film structures with much improved selectivity for solar thermal applications. J Applied Physics Letters 1992; 60(5): 545-547.
<http://dx.doi.org/10.1063/1.106602>
- [26] Dan A, Jyothi J, Chattopadhyay K, Barshilia HC and Basu B. Spectrally selective absorber coating of WAIN/WAION/Al₂O₃ for solar thermal applications. J Solar Energy Materials and Solar Cells 2016; 157: 716-726.
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