



Characterization of magnetron sputtered sub-stoichiometric CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ coatings



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ABSTRACT

The influence of varying nitrogen and oxygen partial pressures on microstructure, mechanical and optical properties of magnetron sputtered CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ coatings has been studied. The partial pressure of nitrogen reactive gas was varied from 0.037 Pa to 0.15 Pa for CrAlSiN_x films, and the N_2/O_2 (85%:15%) partial pressure was varied from 0.046 Pa to 0.21 Pa for $\text{CrAlSiO}_y\text{N}_x$ layers. Transmittance and reflectance of samples were measured and were modeled to obtain the spectral optical constants, n and k . Chemical state, composition, morphology and microstructure of films were analyzed by XPS, RBS, XRD, Raman Spectroscopy and SEM. Films' hardness was evaluated using nanoindentation method. XRD results revealed that the two samples CrAlSiN_x with $P_N = 0.15$ Pa and $\text{CrAlSiO}_y\text{N}_x$ with $P_{NO} = 0.21$ Pa are polycrystalline with cubic (fcc- B_1) structure. On contrary, all other films prepared with lower reactive gases partial pressures are amorphous. The chemical composition changed with the variation of reactive gases partial pressure, although the Cr: Al: Si composition ratio remained approximately constant, 1.25:1.5:1. All samples showed low hardness, mainly due to lower content of reactive gases and higher content of Si. However, the sample CrAlSiN_x with $P_N = 0.15$ Pa has the highest value of 11.1 GPa. Optical constants are seen to be very sensitive to reactive gases partial pressure. The refractive index and extinction coefficient were lower for coatings with higher reactive gases partial pressure. These coatings are good candidates for designing selective solar absorber stacks for different applications.

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1. Introduction

CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ are examples of multi-elemental thin films [1]. Recently, enormous studies and technological efforts have been devoted to the research on those kinds of materials, due to their excellent properties and numerous industrial applications. Chromium nitrides, oxides and oxy-nitrides generally have high oxidation resistance [2–9], chemical and thermal stability at high temperature [10–15], good thermal diffusion barrier [16], good corrosion resistance [17] and high hardness [18–22]. The numerous applications are divided into two main groups. First one is the optical and electrical applications such as, optical detectors, sensors, optical filters, lenses, emitting diodes, on concentrating solar power (CSP) [23–28] and phase shifting masks [29,30]. The second group is for plastic metal molds, cutting and drilling tools [31,32], due to their high hardness and wear resistance. This paper is devoted to study the influence of varying nitrogen and oxygen partial pressures on microstructure, mechanical and optical properties of sputtered CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ coatings in the sub-stoichiometric

range, where the ratio $(O + N) / (Cr + Al + Si)$ is lower than 1. In literature [33,34], it is found that hard nano-composite coatings based of nc- CrN/a-SiN_x are optically opaque. This would be enough for a coating with high solar absorption, but not sufficient to have a coating with low emissivity. On the other hand, adding aluminum to Cr-Si-N changes the grain size, the composition and the mechanical properties of those materials, and tend to be amorphous and more transparent. This leads to an improvement of oxidation resistance properties and opens the possibility to tune the optical properties. Moreover, Oxygen content in films affect the whole coating properties, as an example, if oxygen content in oxynitrides increase, then films will be more transparent with lower refractive index, because of losing of their metallic behavior. Also, hardness values of such coatings remain low (12–13 GPa) in the range of oxygen ratio $[O]/[O + N]$ of 20%–50% in films as reported by Karimi et al. [1] [8]. So, adjusting oxygen and nitrogen contents enables to control the optical, chemical, mechanical and electrical properties of CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ coatings within a wide range [1,8,35,36]. Despite there are a lot of studies about nitride and oxy-nitrides, only limited researches focus on sputtered CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ coatings. However, for these coatings exist in the literature devoted to the microstructure or mechanical properties studies.

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The main objective of the present work is to understand the optical properties of these coatings as varying reactive gases pressure, such that it can be used in structural designs of solar selective absorber stacks for high temperature applications. In addition, to study the influence of varying nitrogen and oxygen partial pressures on microstructure, mechanical properties of the coatings.

2. Experimental

A series of thin individual layers of CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ were deposited on glass substrates with different nitrogen and oxygen partial pressures as reactive gases, as shown in Table 1. These thin layers were used to track the influence of varying those partial pressures upon optical properties of sputtered CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$. For morphology, chemical composition, crystalline structure and mechanical properties studies, thicker samples were deposited on (100)-oriented silicon wafer (used for SEM, XRD, XPS and RBS analysis) and polished stainless-steel substrates (used for nanoindentation tests) with same parameters as thinner ones, as shown in Table 2. Silicon wafer and stainless-steel substrates were ultrasonically cleaned in acetone for 15 min. The depositions were performed at room temperature in a vacuum chamber which evacuated up to 2×10^{-4} Pa base pressure. A pulsed dc bias of -60 V (frequency 90 kHz) was applied to the substrate holder during all depositions. The deposition times were fixed as 1 min and 30 min for thin and thick layers, respectively. The target (Chromium-Aluminum, 70–30 at% with nine 1 cm diameter silicon discs, 99.9% purity) was sputter cleaned in Ar atmosphere for 3 min. An additional Ar ion etching step was implemented for 15 min to clean the substrates using a voltage of -500 V. The target current density was 6.2 mA/cm^2 , and the argon flow was adjusted to reach a constant total pressure of 0.37 Pa.

The crystalline structure of the samples was analyzed by using X-ray diffraction employing a Bruker AXS Discover D8 operating with $\text{Cu K}\alpha$ radiation. The measurements were performed at an incidence angle of $\alpha = 3^\circ$. Scanning electron microscopy (SEM) was performed with a Nano SEM-FEI Nova 200(FEG/SEM) microscope. Energy dispersive X-ray spectroscopy (EDS) analyzes were performed with the electron beam of the SEM, with an energy of 10 keV (EDAX – Pegasus X4M system). Nanoindentation tests were performed by using nano/microindentation-Micro Materials equipment, that has: load range up to 500 mN, load resolution 50 nN, depth range 0–50 mm and contact force <5 mN. Nanoindentation tests were applied with maximum loads ranged between 6 and 8 mN. Then, hardness and elastic modulus data were obtained using the method proposed by Oliver and Pharr [37]. The measurements were repeated five times for each specimen. Raman scattering measurements were carried out on alpha300 R confocal Raman microscope (WITec) using a 532 nm Nd: YAG laser for excitation. The system was operated with an output laser power of 2.5 mW. The laser beam was focused on the sample by a $\times 50$ lens (Zeiss); and the spectra were collected with a 600 groove/mm grating using 5 acquisitions with a 2 s acquisition time. Rutherford back scattering (RBS) measurements were done at the CTN/IST Van de Graaff

accelerator at the small chamber were three detectors are installed: standard at 140° , and two pin-diode detectors located symmetrical to each other, both at 165° . Spectra were collected for 2 MeV $^4\text{He}^+$, and 2.3 MeV $^1\text{H}^+$. Normal incidence was used in the experiments and the obtained data were analyzed with the IBA Data Furnace NDF [38]. Chemical composition and chemical bonding were evaluated using X-ray photoelectron spectroscopy (XPS). The measurements were performed using a Kratos AXIS Ultra HSA X-ray photoelectron spectroscopy (XPS) system, with an $\text{AlK}\alpha$ (1486.7 eV) X-ray source and with 40 eV pass energy. Binding energy was referenced to the C 1 s peak position at 285.0 eV to avoid the influence of the electro-static charging effects of samples. Data analysis and peaks fitting of the XPS spectra were performed by using the CasaXPS software with Shirley background and GL(30)line shape¹ [39].

Optical measurements, in transmittance and reflectance modes, were performed in the wavelength range of 250–2500 nm, using a Shimadzu PC3101 UV–VIS–NIR scanning spectrophotometer. The reflectance measurements were performed at an incidence angle of 8° using an integrating sphere attachment and an Al mirror as a reference. The reflectance data were corrected according to the Al-reference reflectance curve.

3. Results and discussion

3.1. Optical properties

Fig. 1 shows the transmittance (T) and reflectance (R) spectra of CrAlSiN_x deposited at different N_2 partial pressure, from 0.037 Pa to 0.15 Pa and of $\text{CrAlSiO}_y\text{N}_x$ films deposited at different N_2/O_2 partial pressure, from 0.046 Pa to 0.21 Pa.

The results presented in Fig. 1a show that the CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$ layers become more transparent and lose their metallic behavior as the nitrogen and oxygen partial pressures increase. This is mainly due the presence of to Al and Si nitrides and oxides, which are transparent. In accordance with this, the reflectance in the same wavelength range decreases with increasing nitrogen and oxygen partial pressures. The optical constants, refractive index (n) and extinction coefficient (k), and layers thicknesses were determined from (T) and (R) curves [40] by using optical simulation program SCOUT [41]. These thicknesses were used to calculate the deposition rates shown in Table 1, which are slightly lower than those calculated by using the thicknesses of thicker samples, measured by SEM that shown in Table 2. Fig. 2 shows the optical constants, refractive index (n) and extinction coefficient (k), as a function of wavelength in the range of 250–2500 nm, which were obtained from the modeling of experimental T and R spectra. The results shown in the figure indicate a general behavior of n and k with a decrease as increasing the gases partial pressures for both nitride and oxynitride layers. Increasing oxygen and nitrogen amount in films caused an increment in its fraction bonds with other metals in films. Moreover, it is seen that the refractive indices for the CrAlSiN_x layers increase in the wavelength range 250–1000 nm, which make these layers appropriate materials for selective absorption of solar radiation and other optical applications. The refractive index of $\text{CrAlSiO}_y\text{N}_x$ layers also shows a similar behavior with wavelength, but for higher gases partial pressures it becomes almost constant. The oxygen induces a decrease in both, the refractive index and extinction coefficient, for values that is not possible to get with nitride. For example, the minimum refractive index for nitrides is higher than 2.5, while with oxynitrides it is possible to tune it down to 1.6. A similar effect can be seen for the extinction coefficient, where in oxynitrides can be tuned down to zero, while in nitrides is always higher than 0.2. This behavior is also related with the Cr amount, which cannot be below a

Table 1

Oxygen and nitrogen partial pressures of reactive gases in deposition for thin single layers (<100 nm) used to track the optical properties of sputtered CrAlSiN_x and $\text{CrAlSiO}_y\text{N}_x$. Deposition rates were calculated using SCOUT software.

Nitride layer	N_2 partial pressure (Pa) ^a	Deposition rate [nm/min]	Oxynitride Layer	N_2/O_2 (85:15) partial pressure (Pa) ^a	Deposition rate [nm/min]
1	0.037	47.0	1	0.046	45.9
2	0.051	37.6	2	0.064	42.1
3	0.056	35.9	3	0.068	40.6
4	0.060	33.7	4	0.075	38.8
5	0.071	31.0	5	0.092	28.7
6	0.15	17.3	6	0.21	18.6

^a P_{NO} will be used in instead of N_2/O_2 (85:15) Partial pressure and P_N instead of N_2 Partial pressure.

¹ GL (p): Gaussian/Lorentzian product formula where the mixing is determined by $m = p/100$, GL (100) is a pure Lorentzian while GL (0) is pure Gaussian.

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