Tanzania Journal of Science 48(3): 660-667, 2022
ISSN 0856-1761, e-ISSN 2507-7961

Effects of Multilayer Structure on the Microstructure and Optical Properties of the DC Sputtered Chromium Thin Films for Selective Solar Absorber Applications

Justine J Tibaijuka[1*], Margaret E Samiji[1], Mmantsae Diale[2] and Nuru R Mlyuka[1]
[1]*Physics Department, University of Dar es Salaam, P.O. Box 35063, Dar es Salaam Tanzania*
[2]*Physics Department, University of Pretoria, Private Bag X20, Hatfield 0028 South Africa*
**Corresponding author, emails: jtibaijuka14@gmail.com, justine.tibaijuka@udsm.ac.tz*
Received 13 Apr 2022, Revised 29 Sep 2022, Accepted 30 Sep 2022, Published Sep 2022
DOI: https://dx.doi.org/10.4314/tjs.v48i3.13

Abstract

Chromium thin films exhibit several properties that make them potential for solar thermal applications. In this work the effect of film thickness and sputtering power based multilayer structure on the optical properties of DC sputtered chromium thin films is reported. The structural, topological, and optical properties of these films were determined by X-ray diffractometer, Atomic Force Microscopy, and Ultraviolet-Visible-Near Infrared spectrophotometer, respectively. XRD spectra revealed a single peak with preferential orientation of (200) and (210) for single layer and multilayer chromium films, respectively. The grain size and roughness were relatively higher for the multilayer compared to single layer Chromium films. Spectral transmittance showed very high sensitivity to film thickness with average peak of 69% and 5% at a wavelength range of 250-2500 nm for the film thickness of 12 nm and 94 nm, respectively. Spectral transmittance was also found to be higher in single layered films than multi-layered films. Findings from this study suggest that multilayer structure have the potential of tuning the microstructure and optical properties of low thickness Cr films, hence, extending its potential applications in selective solar absorber applications.

Keywords: Multilayer, Chromium, Sputtering, Optical constants

Introduction

Chromium (Cr) and its corresponding oxides are among the most researched and used thin films due to their diverse and prospective properties. These properties include good adhesion, high melting point, high hardness, high wear and corrosion resistance, low density and high thermal conductivity that are very important for wide and diverse range of applications (Kulkarni and Chang 1997, Lovrinčić and Pucci 2009). Cr based thin films have many applications including corrosion protection, photo masks, optical beam splitters, and in selective solar absorber applications to mention few (Foroughi-Abari et al. 2012, Bikulčius et al. 2017, Salo et al. 2020, Kuo et al. 2020). Furthermore, Cr possess an intrinsic spectral selectivity that can be tuned by employing different deposition methods and conditions thus making it a potential for novel design of selective solar absorbers (Jingxue et al. 2016).

A variety of methods are reported for coating these films including chemical vapour deposition, pulse laser deposition, spray pyrolysis, sol gel spin coating, thermal evaporation and sputtering. Among these methods, sputtering is versatile and suitable for large area deposition due to its relatively high deposition rate and being environmentally friendly (Höflich et al. 2016, Singh et al. 2018). Most of thin films produced by this method have high-quality uniform films with exceptional physical and optical properties (Ollotu et al. 2021).

In most cases, metallic thin films employed in selective solar absorber coatings are deposited as single layer and their optical and microstructural properties could be modified by adjusting the deposition parameters and conditions. However, in some cases, the films could be deposited as multilayer structure and their microstructure and optical properties could be modified by varying the deposition conditions such as number of individual layers, film thickness, and deposition power among the layers in a multilayer configuration. The later deposition approach is reported to be essential in modifying the properties of thin films such as adhesion of the films on a substrate and enhancement of spectral selectivity due to multiple reflections and interferences occurring between the layer interfaces. Besides, multilayer structure has been reported to minimize the residual stress in some film coating (Jingxue et al. 2016). Residual film stress is one of the prominent defects in thin film solids deposited by Physical Vapor Deposition (PVD) methods attributed to unbalanced equilibrium processing conditions. Depending on intended final properties of the coating, residual film stress could either positively or negatively influence the performance of a coating as high level of stress favours several detrimental interfacial issues, such as buckling or cracking which may cause poor adhesion of film coating and hence affecting the performance of spectral selective device (Guilbaud-Massereau et al. 1995, Höflich et al. 2016). Thus, controlling the level of residual stress in film coatings is still vital in designing and developing high quality selective absorber coatings. Along with the improvement made in microstructure and optical properties of Cr, still the systematic research about the effects of structural design and the deposition conditions particularly multilayer structure deposited at different powers on microstructure and optical properties which are essential for spectral selective of Cr thin films is lacking.

In this study therefore, two different growth configurations were adopted in which three thin layers of Cr films were deposited consecutively at different powers and their results are compared with single Cr film of the same thickness. The influence of thickness on the optical properties was investigated as well.

Materials and Methods

The deposition of both single and tri-layered Cr thin films onto soda lime glass (SLG) substrates were achieved at room temperature by DC magnetron sputtering of high purity Cr target (99.99%) from Plasmaterials Inc. Prior to deposition, SLG substrates with dimensions of 72 mm x 25 mm were first cleaned ultrasonically then rinsed in distilled water and ethanol, before being suspended in ethanol vapour. The deposition chamber was evacuated to the ultimate base pressure of 6.8 x 10^{-6} mbar using turbo molecular pump bucked up by rotary mechanical pump before deposition. For single layer, the sputtering was done at a power of 25 w and working pressure of 3.6 x 10^{-3} mbar using high purity argon gas (99.99%) flowing at a rate of 15 sccm and the thickness of 32 nm was achieved. For tri-layer, sputtering was achieved using the same conditions as those for single layer except the sputtering power that was set at 25 w/50 w/75 w for the consecutive layers while maintaining the overall thickness as that of single layer. The thickness of each individual layers in multilayer stack was set to 10/11/11 nm and was achieved by using the prior optimized deposition rates. In both cases, the substrate-target distance was set to 12 cm. After deposition, the films were analysed for structural, morphological and optical properties. Films' thicknesses were determined by using the Alpha Step surface profiler that measured a step created using a Teflon tape stacked on a substrate prior to film deposition. The surface morphology of the films was investigated with the help of Nanoscope IIIa Multimode AFM set in taping mode using RTESP7, 125 µm pyramidal silicon tips for a scan size of 1 x 1 µm at a scan rate 2 Hz. The obtained images were processed and analysed using Gwydion software (Nečas and Klapetek 2012) and WSxM software (Horcas et al. 2007), respectively. The structural properties of the films were determined using an X-ray Diffractometer (XRD) in which Cu K-alpha radiation of 0.1504 nm wavelength was used. The value of Full Width at Half Maximum (FWMH) of the dominant XRD peak was determined by fitting the dominant peak using origin lab Pro 2018 software. The crystalline phases were identified by comparing the measured Bragg diffraction peaks with the corresponding cards provided by ICDD. The transmittance and reflectance in the wavelength range 250-2500 nm were measured using a double beam Perkin Elmer Lambda 1050+ UV/VIS/NIR spectrophotometer. The optical constants were determined through fitting of theoretical and measured transmittance and reflectance data using Scout software (2.4, WTheiss Hardware and Software) as ascribed by Khelifa et al. (2019).

Results and Discussion

XRD and AFM analysis

Figure 1 shows the X-ray diffraction patterns of a 32 nm as deposited Cr thin films. The patterns depict only one diffraction peak at 2Θ ≈ 44.2° for multilayer and 2Θ ≈ 39.3° for single layer film indicating the preferential orientation on (210) and (200) planes, respectively (PDF No: 19-0323). The observed shift of peak position to lower angles may be associated with residual stress due to the increase in deposition power (Wang et al. 2011, Höflich et al. 2016, Ollotu et al. 2020). The structural transformation of Cr films was also observed by other researchers due to other processing parameters such as substrate temperature, operating pressure, and substrate biasing (Balu et al. 2005). The average crystallite size of single layer and multilayer Cr films were computed using the Debye-Scherer formula as per equation 1.

$$D = \frac{0.94\lambda}{\beta\cos\theta} \qquad (1)$$

Where: D, λ, β and θ are crystallite size, XRD radiation wavelength, Full-Width at Half Maximum (FWHM) of a dominant peak and Bragg angle, respectively. The FWHM of the diffraction peaks reveals the larger crystalline size for single layer than multilayer Cr films (Table 1). The broadening of diffraction peaks for multilayer Cr films is attributed to the deterioration of the crystallinity of the films due to the formation of stress (Lekshmy et al. 2013). These findings suggest that the multilayer stack is potential for structural transformation and residual stress engineering (Balu et al. 2005, Peralta et al. 2020) that might be of interest in tuning the spectral selective and stability of Cr coating for solar thermal applications.

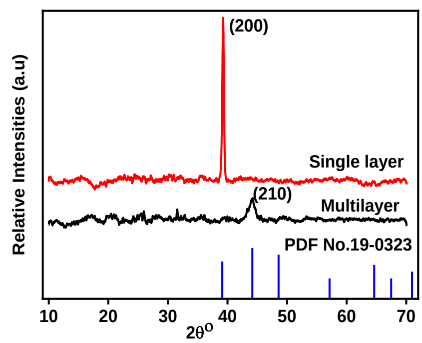

Figure 1: The XRD spectra for single layer and multilayer Cr thin films showing a shift in the preferred crystal orientation.

Table 1: FWHM, crystallite size (D), peak position (2Θ˚) and planar distance (d) and lattice constant for Cr thin films

Sample ID	No. of layers	2Θ(˚)	FWHM (°)	D (nm)	(hkl)
Single layer	1	39.2	0.34	0.434081	(200)
Multilayer	3	44.2	1.29	0.115957	(210)

Figure 2 shows 2D and 3D AFM topographical images of the as deposited single layer and multilayer chromium thin films. It was observed that the surface morphology is changed by number of layers deposited at different power. AFM micrographs reveal the small cluster of grains for both single layer and multilayer chromium films, though the single layer film has smaller grains relative to multilayer film. The difference in trends between the XRD and AFM data sterns from the fact that XRD measures the size of crystallite while AFM determines the grains size. The micrographs further reveal the increase of root mean square (RMS) and the average roughness from 2.8 nm and 2.1 nm for single layer film to 4.3 and 3.6 nm for multilayer films, respectively. The surface roughness plays an important role on the quality and surface texture of the deposited films. The increase of roughness observed was associated with the decrease in homogeneity of the film due to nucleation of particles with the increase in number of layers.

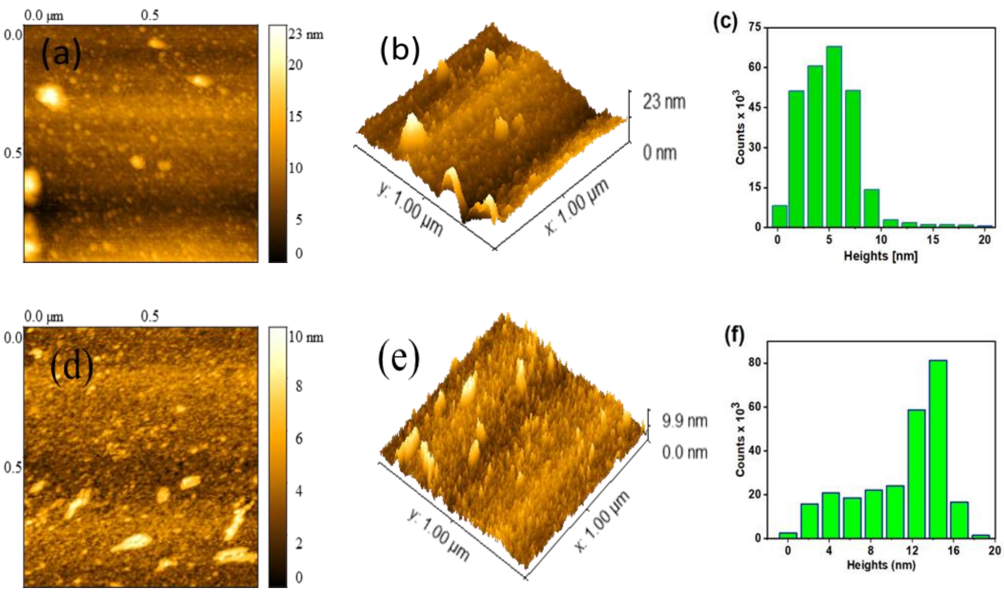

Figure 2: 2D and 3D AFM images with corresponding surface height distributions for Cr thin films (a-c) single layer (d-f) multilayer.

Table 2: Surface parameters for Cr thin films analysed by AFM

Sample ID	No. of layers	Roughness (nm)	RMS (nm)	Kurtosis	Skewness
Single layer	1	2.1	2.8	6.9	1.2
Multilayer	3	3.6	4.3	2.5	-0.8

Table 2 indicates the skewness (Ska) and kurtosis extracted from the surface height distribution histogram of the measured samples (Figure 2 c and f). The skewness and kurtosis measurements are important parameters for determining the symmetry and sharpness or 'peakedness' of surface height distribution values, respectively (Eaton and West 2010). The skewness values of 1.2 and -0.8 were recorded for single layer and multilayer films, respectively indicating the substantial skewed distribution. The skewness was found to lie on the positive value for single layer and on negative value for multilayers signifying a considerable height values above the average for single layer and considerable height below the average for multilayer. This suggests the average surface height in single layer was dominated by peaks while the average surface height was dominated from valleys in multilayers (Malik and De la Hidalga-Wade 2015). Moreover, the kurtosis values of 6.9 and 2.5 were recorded for single layer and multilayer films, respectively indicating that single layer films had narrower and sharper surface height distributions than multilayer Cr films.

Optical properties

Figures 3(a) and 5(a) show the transmittance spectra of the deposited single layer and multi-layer Cr films. The average transmittance of films decreased with the increase in thickness. Furthermore, the single layer exhibited higher average transmittance than the multilayer of the same thickness (Figure 5a).

The refractive indices (n) and extinction coefficients (k) of the deposited thin films were determined by fitting the theoretical and experimental transmittance and reflectance into Scout software using suitable dielectric models as depicted in Figures 3(c-d) and 5c. As seen from Figures 3c-d and 5c, the obtained refractive indices show decreasing trends with wavelength, concurrently the obtained extinction coefficients showed increasing trends with wavelength indicating the metallic behaviour of Cr metal (Khelifa et al. 2018). The films' average solar transmittances, T_{av} were determined by Equation (2) using Air Mass 1.5 solar irradiance G(λ) as ascribed by Maghanga et al. (2010) and Ollotu et al. (2020).

$$T_{av} = \frac{\sum_{250}^{2500} T(\lambda)G(\lambda)}{\sum_{250}^{2500} G(\lambda)} \tag{2}$$

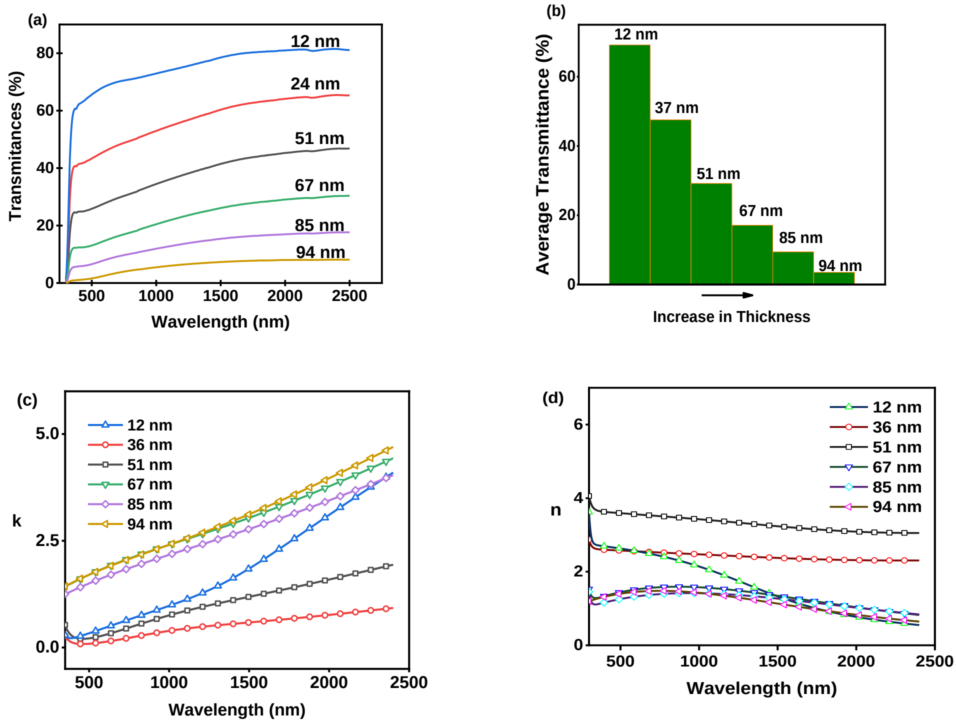

Figure 3: Optical transmittance (a) of as-deposited Cr thin films with different thickness deposited at a power of 25 w and Argon pressure of 15 sccm and their corresponding average transmittance (b), extinction coefficient (c) and refractive index (d).

Figure 4 shows the reflectance spectra of the deposited chromium thin films. All films exhibited a reflectance below 40%, and similarly the reflectance of the film were increasing with the increase in thickness. Furthermore, the single layer exhibited lower reflectance than the multilayer of the same thickness (Figure 6). These findings suggest that the multilayer fabrication approach in this work is potential for tuning the optical properties of Cr thin films while maintaining the lower thickness required in enhancing spectral absorption in the solar spectral range while suppressing infrared emission associated with larger thickness in selective solar absorbers.

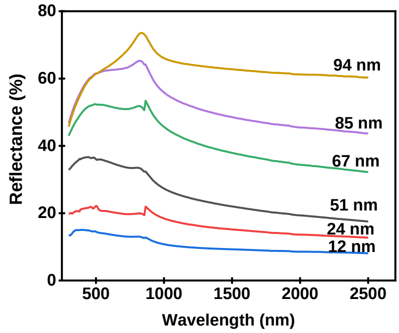

Figure 4: Reflectance of as deposited Cr thin films with different thickness deposited at 25 w powerand Argon flow rate of 15 sccm.

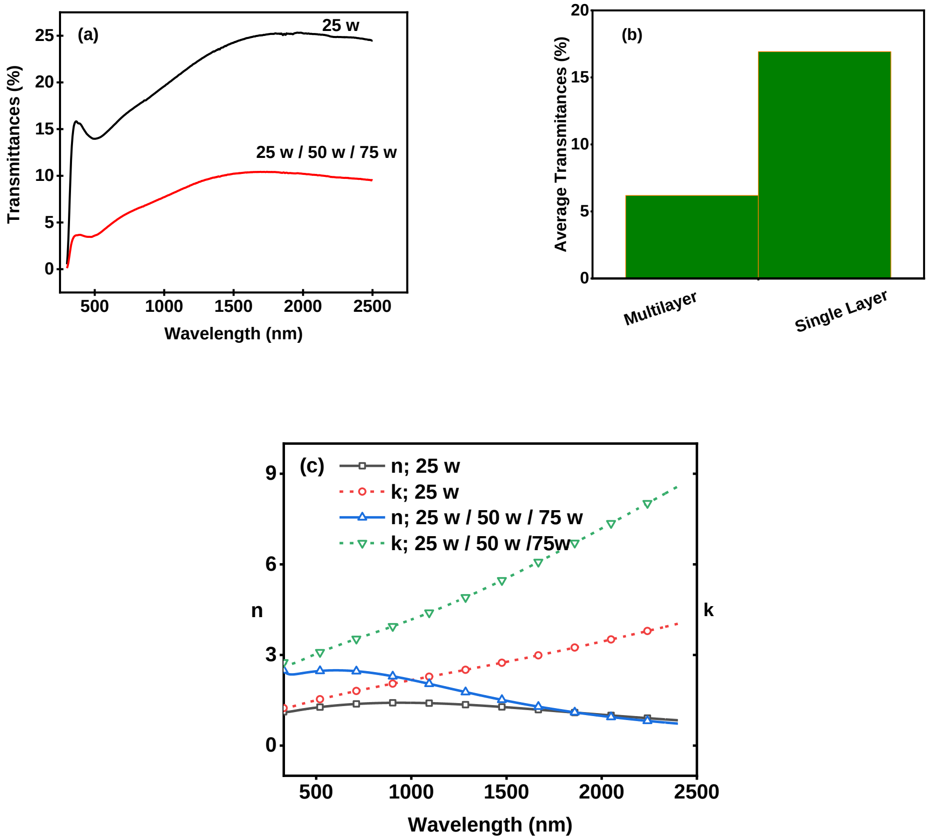

Figure 5: Optical transmittance (a) of as-deposited single layer and multilayer Cr films and their corresponding average transmittance (b) and optical constants (c).

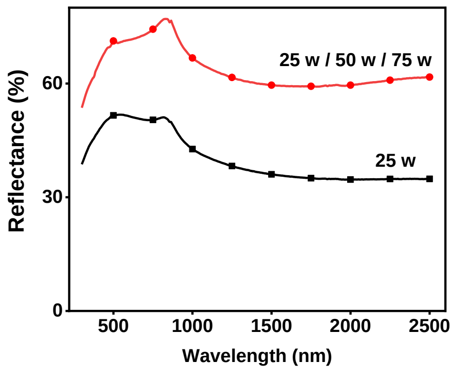

Figure 6: Reflectance of as deposited single and multilayer Cr films deposited at different sputtering powers.

Conclusions

The findings from this study reveals that tuning and transformation of structural, morphology and optical properties for lower thickness Cr coatings could be achieved by employing the power based multilayer structural to suit some of the requirements of spectral selective coating. XRD diffractograms revealed a single diffraction peak for all the chromium films with a preferential orientation of (200) and (210) for single layer and multilayer, respectively and the crystallite sizes of multilayer were larger when compared with single layer. AFM micrographs revealed the relatively high RMS and the average roughness in multi-layered than single layered film. The optical transmittance was higher in single layered films than multi-layered films. Furthermore, the transmittances were found to decrease with thickness while reflectance were increasing with thickness. These results signify that the multilayer deposition approach has significant influences on the microstructure and optical properties of Cr thin films, and thus it has a potential in tuning the structural and optical properties of Cr films for selective solar absorber applications.

Conflict of Interest

There is no conflict of interest to declare.

Acknowledgment

The authors acknowledge all who supported this work including Ministry of Education, Science and Technology of Tanzania for scholarship, University of Dar es Salaam, Materials Science and Solar Energy Eastern and Southern Africa network (MSSEESA) and International Science Programme (ISP)-Uppsala University, Sweden for research materials and facilities support.

References

Balu R, Raju AR, Lakshminarayanan V and Mohan S 2005 Investigations on the influence of process parameters on the structural evolution of ion beam sputter deposited chromium thin films. *Mater. Sci. Eng.: B.* 123(1): 7-12.

Bikulčius G, Češuniene A, Selskiene A, Pakštas V and Matijošius T 2017 Dry sliding tribological behavior of Cr coatings electrodeposited in trivalent chromium sulphate baths. *Surf. Coat. Technol*. 315: 130-138.

Eaton P and West P 2010 Atomic force microscopy. Oxford University Press.

Foroughi-Abari A, Xu C and Cadien K C 2012 The effect of argon pressure, residual oxygen and exposure to air on the electrical and microstructural properties of sputtered chromium thin films. *Thin Solid Films* 520(6): 1762-1767.

Guilbaud-Massereau V, Celerier A, Machet JJ 1995 Study and improvement of the adhesion of chromium thin films deposited by magnetron sputtering. *Thin Solid Films*. 258(1-2): 185-193.

Höflich A, Bradley N, Hall C, Evans D, Murphy P, Charrault E 2016 Packing density/surface morphology relationship in thin sputtered chromium films. *Surf. Coat. Technol.* 291: 286-291.

Horcas I, Fernández R, Gómez-Rodríguez JM, Colchero J, Gómez-Herrero J and Baro AM 2007 WSXM: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* 78(1): 013705.

Jingxue F, Zhao W, Wei W, Ye Y, Lin Z, Xin W, Ruijiang H, Hui S, Chen MZ 2016 Preparation and optimization of a molybdenum electrode for CIGS solar cells. *AIP Adv*. 6(11): 115210.

Khelifa AB, Khamlich S, Nuru ZY, Kotsedi L, Mebrahtu A, Balghouthi M, Guizani AA, Dimassi W and Maaza M. 2018 Growth and characterization of spectrally selective $Cr_2O_3/Cr/Cr_2O_3$ multilayered solar absorber by e-beam evaporation. *J. Alloys Compd*. 734: 204-209.

Khelifa AB, Soum-Glaude A, Khamlich S, Glénat H, Balghouthi M, Guizani AA, Maaza M, Dimassi W. 2019 Optical simulation, characterization and thermal stability of $Cr_2O_3/Cr/Cr_2O_3$ multilayer solar selective absorber coatings. *J. Alloys Compd.* 783: 533-544.

Kulkarni AK and Chang LC 1997 Electrical and structural characteristics of chromium thin films deposited on glass and alumina substrates. *Thin Solid Films* 301(1-2): 17-22.

Kuo CC, Lin CH, Lin YT and Chang JT 2020 Effects of cathode voltage pulse width in high power impulse magnetron sputtering on the deposited chromium thin films. *Coatings* 10(6): 542.

Lekshmy SS, Daniel GP, Joy K 2013 Microstructure and physical properties of sol gel derived SnO_2:Sb thin films for optoelectronic applications. *Appl. Surf. Sci.* 274: 95-100.

Lovrinčić R and Pucci A 2009 Infrared optical properties of chromium nanoscale films with a phase transition. *Phys. Rev. B* 80(20): 205404.

Maghanga CM, Jensen J, Niklasson GA, Granqvist CG and Mwamburi M 2010 Transparent and conducting TiO_2:Nb films made by sputter deposition: Application to spectrally selective solar reflectors. *Sol. Energy Mater. Sol. Cells* 94(1): 75-79.

Malik O and De la Hidalga-Wade FJ 2015 Optoelectronics properties of tin-doped indium oxide films fabricated by DC magnetron sputtering in pure argon with post-annealing in oxygen atmosphere. *J. Mater. Res.* 30(12): 1894-1901.

Nečas D and Klapetek P 2012 Gwyddion: an open-source software for SPM data analysis. *Open Phys.* 10(1): 181-188.

Ollotu ER, Mlyuka NR and Samiji ME 2021 Effects of rapid thermal annealing on the properties of room-temperature oxygenated DC sputtered zinc thin films for CZTS solar cells application. *Tanz. J. Sci.* 47(2): 637-647.

Ollotu ER, Nyarige JS, Mlyuka NR, Samiji ME, Diale M 2020 Properties of ITO thin films rapid thermally annealed in different exposures of nitrogen gas. *J. Mater. Sci.: Mater. Electron.* 31: 16406-16413.

Peralta J, Esteve J and Lousa A 2020 δ-A15 and bcc phases coexist in sputtered chromium coatings with moderate oxygen contents. *Thin Solid Films* 693: 137676.

Salo SA, Abdallah B, Akel M and Kakhia M 2020 Structural and plasma characterization of the power effect on the chromium thin film deposited by DC magnetron sputtering. *Optoelectron. Lett.* 16: 369-372.

Singh MM, Vijaya G, Krupashankara MS, Sridhara BK and Shridhar TN 2018 Deposition and characterization of aluminium thin film coatings using DC magnetron sputtering process. *Mater. Today: Proc.* 5(1): 2696-2704.

Wang SF, Lin HC, Bor HY, Tsai YL and Wei CN 2011 Characterization of chromium thin films by sputter deposition. *J. Alloys Compd.* 509(41): 10110-10114.