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# Improved Optical and Mechanical Characteristics of Multilayered $Cu/TiON/CrO_2$ Coating *via* Heat Treatment for Solar Absorbing Applications

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## Abstract

In the last few decades, growing interest has been shown in the development of new solar selective coatings based on transition metal nitride and/or oxinitride for solar absorbing applications. Solar thermal collectors are well thought out to be the most effective process of converting and harvesting solar radiation. In this investigation, Cu/TiON/CrO2 multilayered solar selective absorber coatings have been coated onto Al substrates using the dip-coating process followed by an annealing process at (400, 450, 500, 550, and 600 °C. The XRD analysis showed excellent crystalline quality for the prepared thin films along with enhanced surface features as proved by FESEM images, and the grains are in the range of (27–81) nm. The optical investigations revealed that the film annealed at 600 °C exhibits improved solar absorptance, thermal emittance, and solar selectivity of ~ (90.7 %), (5.8 %) and 15.6, respectively. Also, the highest values of hardness ~ (26.8 GPa) and Young's modulus ~ (250 GPa) were assigned for the film annealed at the highest temperature. Calculated optical band gaps of fabricated thin multilayered $Cu/TiON/CrO_2$ films were found to be in the range of (1.8 – 2.10) eV.

**Keywords**: TiON, Multilayer coatings, Solar selective absorbers, Absorptance, Emittance

## 1. Introduction

So far, advances in technology and science have encouraged researchers and scientists to design new products using simple and cost-efficient processes [1, 2]. In the same way, a need is perceived for the efficient and economical production of thin films on top of suitable substrates for a variety of industrial and technological applications, including optics, catalysts, electronics, sensors, etc.[3, 4]. Transition metal-based thin film coatings have been extensively targeted by researchers to improve their physiochemical, thermal, and mechanical properties. Transition metal nitride and/or oxide coatings demonstrate attractive and desirable optoelectronic, mechanical, physiochemical, and thermal characteristics in a wide range of technological devices [5-8]. These coatings commonly include TiN, TiON, CrN, CrON, MoN, MoON, etc. in their matrices, either as single layer or multilayer coatings. Most of the efforts focus on synthesizing intrinsic or doped single-layer thin films due to their ease of preparation and short working time. However, multilayered transition metal based thin film coatings have recently been overlooked by many researchers and engineers on account of their possessing numerous properties such as exceptional hardness, elastic modulus, adhesion to substrate, good corrosion, wear, and oxidation resistance, in addition to high chemical and thermal stabilities [9, 10].

TiN based thin films have been widely used as solar absorbers. Physical deposition techniques such as thermal evaporation, RF and DC magnetron sputtering, pulse laser deposition, and ion beam deposition were used to produce TiN based solar absorbers despite the expensiveness and sophisticated requirements that include suitable chamber and vacuum systems, which result in overpriced end products [11,12]. Therefore, it becomes very essential to use easy, cheap, and vacuum-free methods to fabricate such kinds of thin film coatings.

The main goal of this work is to investigate the structural, optical, and mechanical properties of multilayered Cu/TiON/$CrO_2$ thin solar absorber films deposited onto aluminium substrates *via* a facile and low cost sol-gel dip coating process.

## 2. Experimental details

### 2.1. Raw materials

Titanium isopropoxide, 98.8%, Sigma Aldrich; copper basis, 98.8%, Sigma Aldrich; chromium nitrate nonohydrate, 97%; Alpha chemika; ammonia, 97%. Merck, phosphoric acid (85%), Carlo Erba Reagents, and ethanol were used as bought. The Cu/TiON/CrO2 thin films were coated onto (25 × 25) mm aluminum substrates after being cleaned in 15% phosphoric acid for 15 minutes and rinsed in deionized water.

### 2.2. Sol preparations and thin film deposition

Appropriate amounts of Ti isopropoxide and chromium nitrate nonohydrate chemicals were separately dissolved in ethanol and stirred at 80 °C for 1h to create 0.1 M of Ti and Cr precursors. Ammonia was then added to the Ti precursor as a source of nitrogen in the TiON matrix.

The thermal evaporation technique was used to deposit Cu layers, which act as back reflectors, onto Al substrates. The Cu films were heated at 150 °C for 1 hour. Then, the TiON layer was coated over the Cu layer by dipping the thin films in Ti precursor, and the process was repeated until the TiON fully covered the Cu layer, followed by heating the films at 150 °C for 1 h. Finally, the CrO2 layer was dip-coated at the top of the thin films using the CrO2 solution. The resultant configurations of Cu/TiON/CrO2 thin films were annealed in the range of 400–600 °C in a step of 50 °C. **2.3.**

**Characterization techniques**

The results of the structural, surface morphology, optical, and mechanical properties of $Cu/TiON/CrO_2$ thin films were collected using XRD analysis, Field Emission Scanning Electron Microscopy (FESEM) images, UV-Vis and FTIR spectroscopy, and nanoindentation measurements, respectively. A BRUKER D8 machine of $CuK_\alpha$ source ($\lambda$ = 1.54 Å) and a Lynx-eyed detector were operated at 40 kV and 30 mA. The XRD data of $Cu/TiON/CrO_2$ thin films was collected in a $2\theta$ range of (25 – 80)°, step size 0.02° and a total time per sample ~20 min.

The morphological features of $Cu/TiON/CrO_2$ thin films were imaged using the Thermo Fisher Scientific F50 FESEM machine. A 3 nm platinum layer was coated onto $Cu/TiON/CrO_2$ thin films to decrease the charging effects.

The UV-Vis reflectance and the FTIR data of $Cu/TiON/CrO_2$ thin films was collected *via* a UV–Vis spectrophotometer (JASCO 670) in the wavelength range of 190 to 2500 nm and a FTIR (Perkin Elmer 100) spectrometer in the range of (2500 – 15000) nm.

Collected reflectance data for synthesized Cu/TiON/ $CrO_2$ thin films was used to calculate the optical parameters, including the solar absorptivity, solar emissivity, absorption coefficient, and energy gaps.

The mechanical properties of $Cu/TiON/CrO_2$ thin films were measured via (CSIRO) Micro Indentation System equipped with a diamond Berkovich indenter. By considering the thin film thicknesses ~ 700 nm, a total load of 5mN was applied to all investigated thin films at an average indentation depth less than 10% of the coating thickness.

## 3. Results and discussions

### 3.1. XRD analysis

**Figure 1** presents the XRD patterns of Cu/TiON/CrO2 thin films. The sharp and intense Bragg's peaks confirm a high degree of crystallinity along with the formation of crystalline features for both TiON and CrO2 phases (JCPDS 87–0633) and (PDF card #841819), respectively. The peak positions of TiON phases located at 2θ values around (36.9, 42.95, 62.5 and 74.8) ° are associated with (111), (200), (113), and (222) reflection planes, respectively [13], while the peaks of CrO2 phases located at 2θ values around (28.7, 37.3, and 56.3) are attributed to (110), (101), and (211) planes, respectively. An improvement in the crystalline quality of Cu/TiON/CrO2 thin films was also observed with increasing annealing temperatures. This could be attributed to the efficient release of the lattice strain in addition to the agglomeration of larger grains around the preferential orientations of both TiON and CrO2 phases [14, 15].

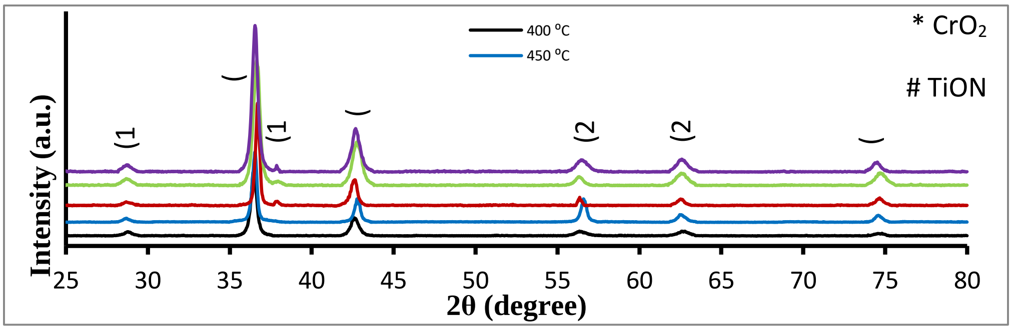


**Figure 1.** XRD patterns of annealed $Cu/TiON/CrO_2$ thin films

The grain sizes and the lattice parameters of synthesized thin Cu/TiON/$CrO_2$ films were calculated using the Scherrer formula, Bragg's equation, and the Bravais lattice system for cubic features [16, 17].

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

$$n\lambda = 2d \sin\theta \qquad (2)$$

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \qquad (3)$$

where ($K$ = 0.9) is a constant, $\lambda$ is the Cu-$K_\alpha$ radiation's wavelength ($\lambda$ = 0.154 nm), $\beta$ is the line broadening at the (FWHM), $\theta$ is the Bragg angle, $a$ is the lattice parameter, and $d$ is the-inter planar distance, ($h\ k\ l$) are Miller indices.

**Figure 2** reveals the variations of the grain sizes of Cu/TiON/$CrO_2$ films with annealing temperature. It is evident that the grain sizes increased with increasing temperature owing to the sufficient energy supplied to the material's atoms to coalesce and be reoriented in the main direction [18,19]. All these result in the formation of a highly crystalline structure, and the film annealed at 600 °C possesses the largest grain size ~ 81 nm among other annealed films. The mean value of the calculated lattice parameter for thin Cu/TiON/$CrO_2$ films was around 4.25 Å which is in agreement with the results reported in the literature for such coatings. **Table 1** presents the detailed structural parameters of Cu/TiON/$CrO_2$ thin films.

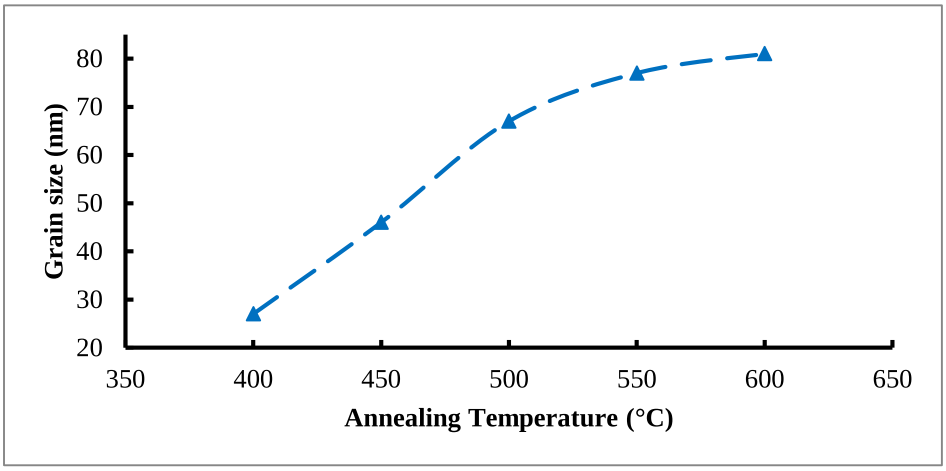


**Figure 2.** Variation of the grain sizes of annealed Cu/TiON/$CrO_2$ thin films with annealing temperatures

**Table 1.** Structural parameters of annealed Cu/TiON/$CrO_2$ thin films

| Annealing temperature (°C) | 2θ (degrees) | d-spacing (Å) | *(h k l)* | Lattice constant (Å) | Crystallite size (nm) |
|---|---|---|---|---|---|
| 400 | 36.44 | 2.46 | (111) | 4.26 | 27 |
| 450 | 36.54 | 2.45 | (111) | 4.25 | 46 |
| 500 | 36.7 | 2.44 | (111) | 4.23 | 67 |
| 550 | 36.64 | 2.45 | (111) | 4.24 | 77 |
| 600 | 36.54 | 2.45 | (111) | 4.25 | 81 |

### 3.2. FESEM images

The surface morphology of fabricated $Cu/TiON/CrO_2$ thin films shows the formation of crystal-like features for all annealed thin films, and the surfaces are dense and uniform as seen in figure 3. Furthermore, the surfaces of annealed $Cu/TiON/CrO_2$ coatings exhibit many agglomerations of smaller particles to form larger grains with a variety of sizes which confirm the results previously noticed in the XRD results.

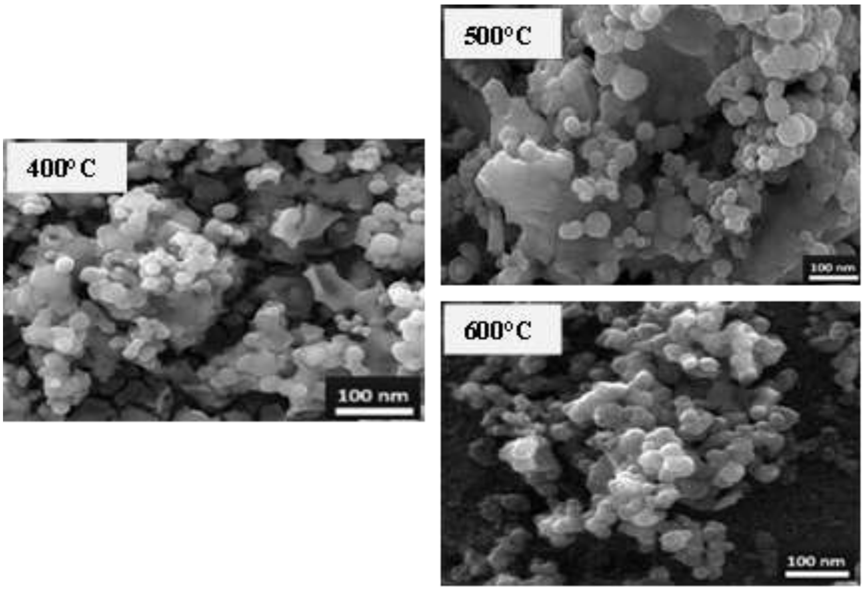


**Figure 3.** FESEM images of annealed $Cu/TiON/CrO_2$ thin films

### 3.3. Optical characterizations of $Cu/TiON/CrO_2$ films

**Figure 4** displays the reflectance spectra of $Cu/TiON/CrO_2$ coatings recorded in the UV-Vis range of (190-2500) nm. The reflectance data was used to estimate the solar absorptance of $Cu/TiON/CrO_2$ thin films using the Duffie – Beckman method [20].

$$\alpha = \frac{\int_{0.19}^{2.5} I_{sol}(\lambda)(1-R(\lambda)d\lambda}{\int_{0.19}^{2.5} I_{sol}(\lambda)d\lambda} \quad (4)$$

It is clearly noticed from Figure 4 that the absorption edges at shorter wavelengths and interference peaks are visible. It is also observed that the absorption edge of the $Cu/TiON/CrO_2$ spectra shifts towards shorter wavelengths with increasing annealing temperature. In order to ideally optimize the reflectance data for solar absorption applications, the reflectance data should be high at longer wavelengths over 2000 nm (called the cut-off region). It has been reported by many researchers that there are three parameters that control the reflectance tendency of TiON-based solar absorbers in the near-infrared region. These parameters are the substrate's reflectivity, the properties of materials involved in the film's matrix, and the film thickness [21, 22].

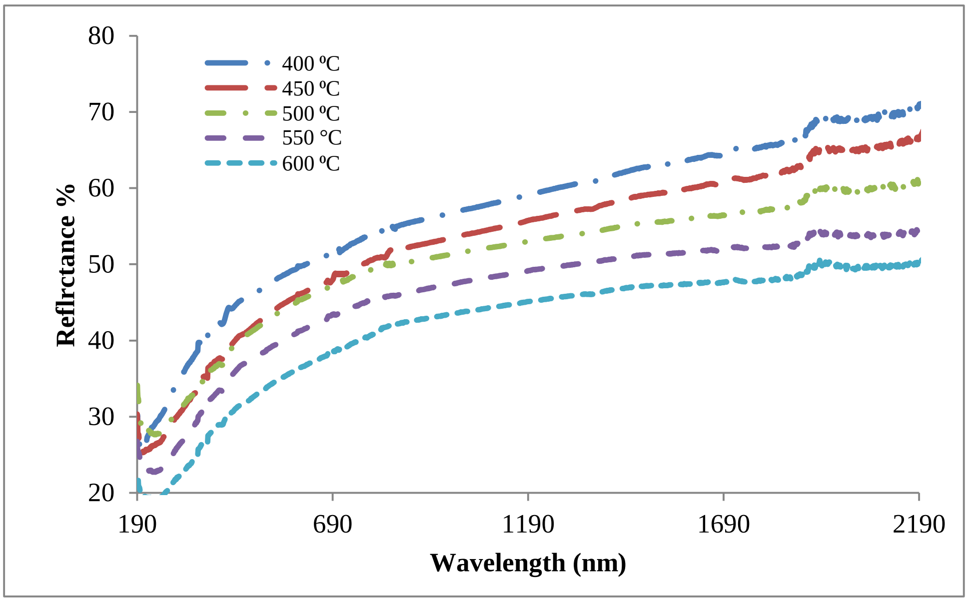


**Figure 4.** Reflectance spectra of annealed Cu/TiON/$CrO_2$ thin films

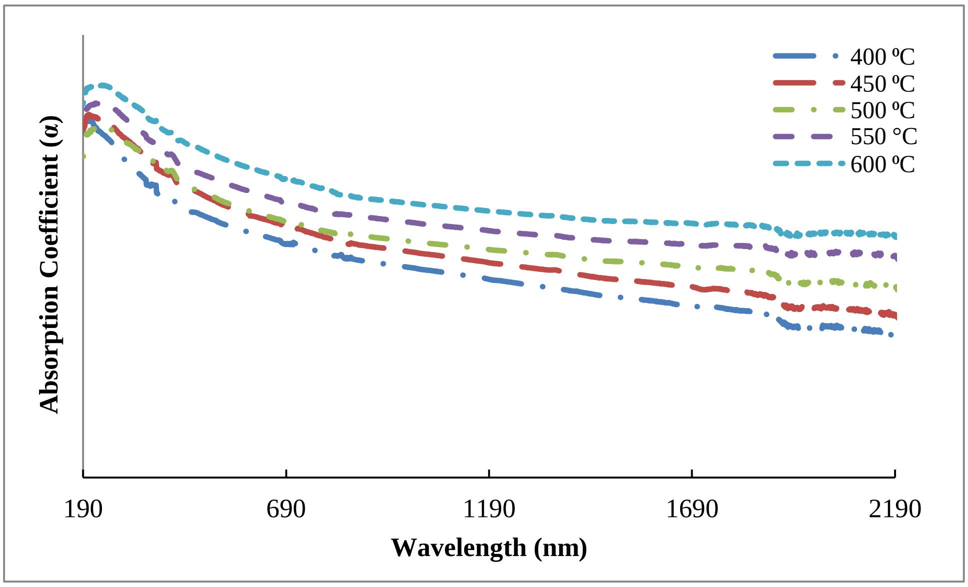


**Figure 5.** Absorption coefficient of annealed Cu/TiON/$CrO_2$ thin films

**Figure 5** presents the absorption coefficient of thin Cu/TiON/$CrO_2$ films. It has been suggested that the solar absorptivity of a matter at a specific wavelength is associated with the exciting of free electrons to higher energy states in the atoms and/or molecules. The Cu/TiON/$CrO_2$ film annealed at 600 °C exhibits the highest absorption coefficient, which results in a solar absorptance ~ 90%. It is well agreed that the higher the solar absorbtance, the better the property for solar selective absorbing devices. It could be accomplished that the well crystallized and developed in addition to the formation of grain-like morphologies in the film structure may promote the sample's surface to absorb as much as possible of the incident radiation *via* numerous reflections that took place between the layers of Cu/TiON/$CrO_2$ thin films and inside the agglomerations and/or at the grain boundaries in the thin film framework [23].

The types of electronic transitions and the energy gabs of synthesized Cu/TiON/$CrO_2$ thin films were estimated using Tauc relation [24-26].

$$\alpha h\nu = B(h\nu - E_g)^n \qquad (5)$$

where, α is the absorption coefficient, $h\nu$ is the photon energy, $B$ is a constant, $Eg$ is the optical band-gap and $n$ is an index depending on the type of optical transition. The energy gaps of annealed Cu/TiON/$CrO_2$ thin films were assessed by extending the linear section of the curves toward the interception point of the x-axis. The estimated energy gaps of Cu/TiON/$CrO_2$ thin films from figure 6 are in the range of (1.8 and 2.1) eV, and the $Eg$ values are inversely dependent on annealing temperature. The lowest observed energy gap around 1.8 eV is linked to the film being annealed at 600 °C due to the development of the structural quality of synthesized Cu/TiON/$CrO_2$ thin films as well as the enhancement of the absorption of incident solar radiation by these coatings. Also, the existence of extended and localized states near the band gap facilitates the absorption of incident solar energy [26].

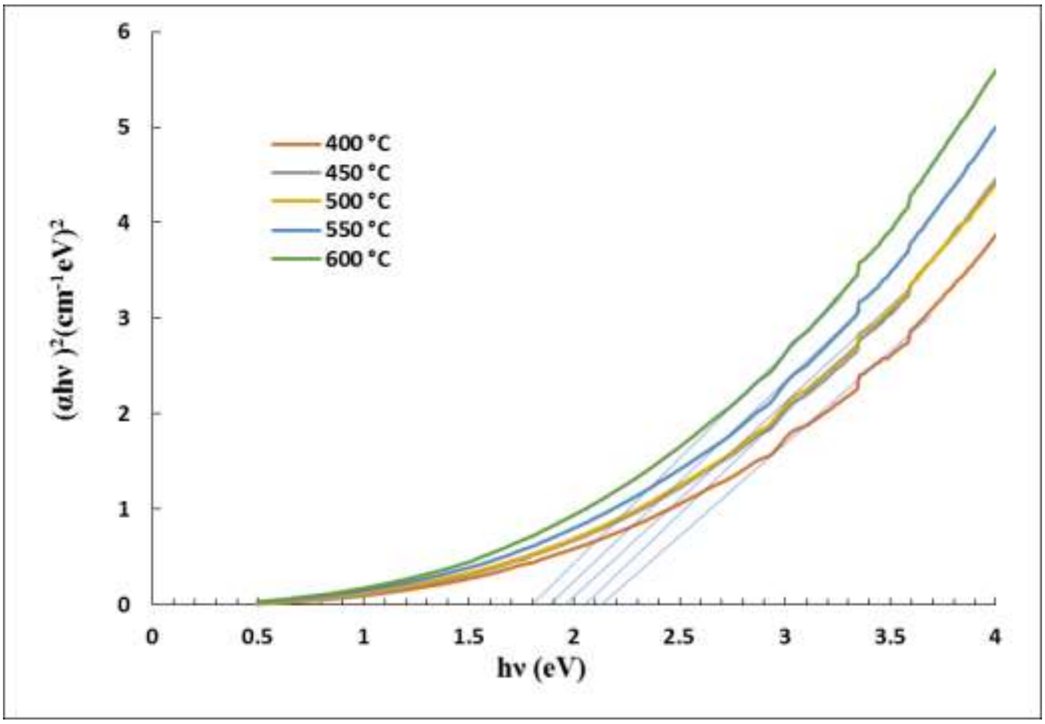


**Figure 6.** Energy band gaps of annealed Cu/TiON/$CrO_2$ thin films

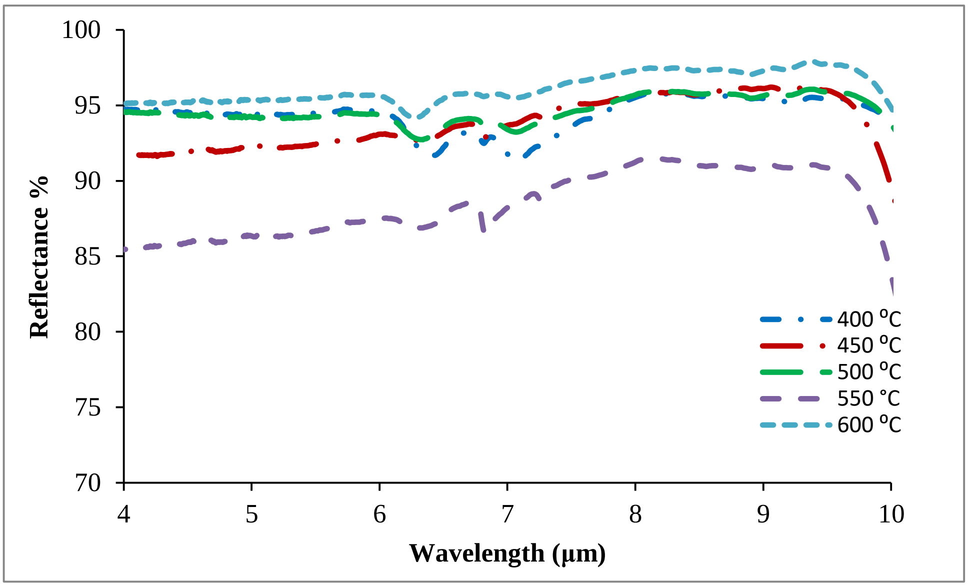


**Figure 7.** FTIR reflectance of annealed Cu/TiON/ $CrO_2$ thin films

FTIR measurements were performed on Cu/TiON/$CrO_2$ thin films in the range of (5 – 15) µm to calculate the thermal emittance, as seen in **Figure 7**. The dependence of thermal emittance on annealing temperature was investigated using the Duffie and Beckman formula [20]. Annealing temperature strongly affected the thermal emittance, and the lowest thermal emittance was assigned for the film annealed at 600 °C. **Table 2** summarizes the optical properties of Cu/TiON/$CrO_2$ thin films.

$$\varepsilon = \frac{\int_{2.5}^{15} I_p\,(\lambda)(1-R(\lambda)d\lambda}{\int_{2.5}^{15} I_p\,(\lambda)d\lambda} \qquad (6)$$

The solar selectivity ($s$) is the main aspect of a solar selective coating and is described as a ratio of the solar absorptivity to the thermal emissivity as defined by the following equation:

$$s = \frac{\alpha}{\varepsilon} \qquad (7)$$

**Table 2.** Optical properties of annealed Cu/TiON/$CrO_2$ thin films

| Annealing temperature (°C) | *Eg (eV)* | α (%) | ε (%) | *S* |
|---|---|---|---|---|
| 400 | 2.10 | 83.0 | 12.4 | 6.7 |
| 450 | 1.96 | 84.8 | 11.6 | 7.3 |
| 500 | 2.0 | 87.4 | 10.3 | 8.48 |
| 550 | 1.90 | 88.8 | 8.1 | 11.0 |
| 600 | 1.80 | 90.7 | 5.8 | 15.6 |

### 3.4. Nanoindentation results

**Figure 8** presents the mechanical properties represented by Young's modulus ($E$) and hardness ($H$) of Cu/TiON/$CrO_2$ thin films. The ($H$) values of Cu/TiON/$CrO_2$ thin films are in the range of (16.5 – 26.8) GPa, while the ($E$) values are in the range of (229 – 250) GPa. Improved mechanical characteristics may be attributed to developing the crystalline quality, thereby decreasing the density of crystal defects such as vacations and voids with increasing annealing temperatures [27, 28].

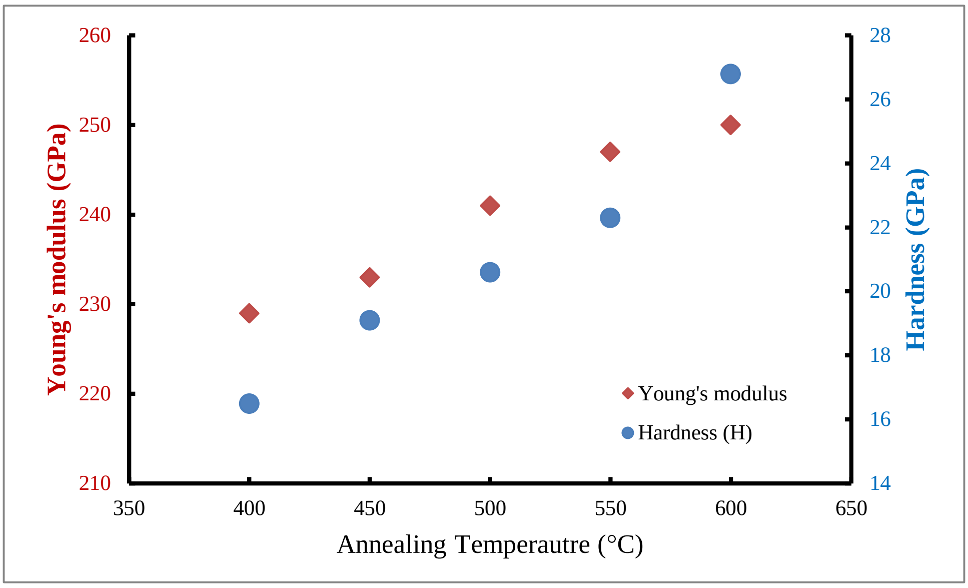


**Figure 8.** Hardness and Young's modulus of annealed Cu/TiON/$CrO_2$ thin films

## 4. Conclusions

Multilayered Cu/TiON/ $CrO_2$ solar selective thin films have been synthesized using a facile sol-gel dip-coating process and annealed in the range of (400 - 600) °C in a step of 50 °C. A good crystallinity and improved surface morphology have been observed for Cu/TiON/$CrO_2$ thin films with crystallized grains in the range of (27 – 81) nm. The optical properties of synthesized thin films show improved solar absorptivity ~ 90.7 and thermal emissivity ~ 5.8 along with band gap energies in the range of (1.8 – 2.10) eV. The mechanical behaviors of Cu/TiON $CrO_2$ thin films were also developed, with the highest values of both harness and Young's modulus at 26.8 GPa and 250 GPa, respectively, for the film annealed at 600 °C. The obtained results for Cu/TiON/$CrO_2$ thin films in this work are recommended for future technological designs in various industrial devices.

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