Indian Journal of Pure & Applied Physics
Vol. 57, March 2019, pp. 175-179

Crystalline TeO_2 thin film with chemical bath deposition

İ A Kariper*
Education Faculty, Erciyes University, 38039, Kayseri, Turkey

Received 7 January 2016; accepted 22 October 2018

Tellurium oxide (TeO_2) crystalline thin film has been produced with chemical bath deposition on substrates (commercial glass). Some properties of the films have been investigated by UV/VIS. The spectrum has been studied in terms of as transmittance, refractive index and reflectivity. The monoclinic and orthorhombic forms have been observed for the structural properties in XRD. The structural and optical properties of tellurium oxide thin films have been analyzed at different pHs of the chemical bath. EDX analysis has been used to determine the elemental ratio of tellurium in the films. Some properties of the films change with deposition pH. The concentration of sodium hydroxide was scanned at 2.5×10^{-3} M, 5×10^{-3} M, 7.5×10^{-3} M and 10×10^{-3} M at pHs of 10, 11, 11.50 and 12, respectively. The optical properties of the films change with the deposition pH of the chemical bath. Also, the film thickness changes with deposition pH at 12, 11.50, 11 and 10 and the respective thickness values are 900, 586, 657 and 866 nm. The optimum parameters have been determined with 10 mL 2.5×10^{-3} M tellurium tetrachloride, 10 mL 2.5×10^{-3} M of potassium hydroxide and 2 mL hydrogen peroxide at pH: 10 for producing γ-TeO_2.

Keywords: TeO_2 thin films, Chemical dropping, Thin film

1 Introduction

Zinc oxide, titanium oxide, etc., are well known transparent thin films and have many applications in technology. Researchers are currently investigating new materials like zinc oxide and titanium oxide for new technologies. Tellurium dioxide (TeO_2) may be a transparent thin film as the others. However it stands out with some special properties and ,s used in such as medical imaging, industrial process monitoring, national security and treaty verification, environmental safety and remediation, and basic science[1-5].

Tellurium oxide has different phases; α-TeO_2, β-TeO_2 and γ-TeO_2. The α-TeO_2 and β-TeO_2 phases are well known structures according to the literature[6]. However researchers have now started working on the γ-TeO_2 structure for gamma radiation and for its properties. Gupta *et al.* produced γ-TeO_2 by RF diode sputtering at room temperature and annealing in the temperature range RT to 400 °C, and the structural and optical properties of the deposited thin films were studied[7]. Frit *et al.* investigated the Raman spectrum and lattice dynamics[8]. Mirgorodsky *et al.*[9] studied the vibrational and structural properties of the glass and crystalline phases of γ-TeO_2.

The aim of this experimental work is to investigate the changes in both the structural and optical properties of γ-TeO_2 thin film and also to discover how to produce the best crystalline γ-TeO_2 thin film. Therefore, tellurium tetrachloride was used in this study and concentration of this compound in aqua was used to determine the optimum parameters of the produced quality crystalline γ-TeO_2 thin films.

2 Experimental

The components of the bath were 2.5×10^{-3} M tellurium tetrachloride and different molarities of potassium hydroxide. Firstly, 10 mL $2.5\text{x}10^{-3}$ M tellurium tetrachloride, 10 mL of different concentrations of potassium hydroxide and 2 mL hydrogen peroxide were added in a beaker which was prepared with ethanol. In order to adjust the pH value of the solution to 10, 11, 11.50 and 12, 2.5×10^{-3}, 5×10^{-3}, 7.5×10^{-3} and 10×10^{-3} M of sodium hydroxide (NaOH), respectively, were added to the solutions. The pH values of the chemical baths were determined using a pH meter (Lenko mark 6230N). The bath was kept for 15 h at 50 °C.

The crystalline structure of the tellurium oxide was confirmed by X-ray diffraction (XRD) with a $CuK\alpha_1$ radiation source (Rikagu RadB model, λ=1.5406 Å) over the range $10^o < 2\theta < 90^o$ at a speed of 3^o min^{-1} with a step size of 0.02^o. The surface properties of all films were investigated using an EVO40-LEO computer

*E-mail: akariper@gmail.com

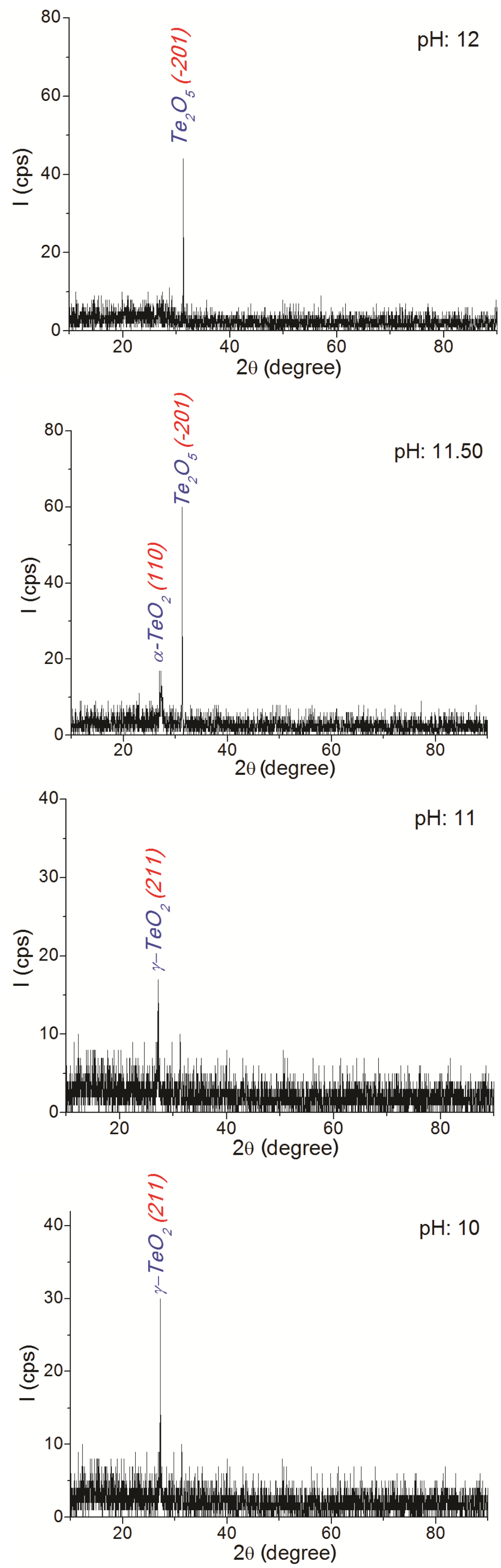

Fig. 1 — X-ray patterns of tellurium oxide films deposited in a bath solution at (a) pH : 12, (b) pH : 11.50, (c) pH : 11 and (d) pH : 10.

controlled digital scanning electron microscope (SEM). Chemical analysis by EDX was performed with an EDX spectrometer attached to the SEM. The film thickness of the films was measured with atomic force microscopy (AFM). The optical measurements were determined by a Lange 500 spectrophotometer at room temperature by placing an uncoated identical commercial glass substrate in the reference beam. The optical spectrum of the thin films was recorded in the wavelength range of 300-1100 nm.

3 Results and Discussion

XRD patterns of tellurium oxide thin films are shown in Fig. 1 and their XRD values at different deposition pHs are shown in Table 1. Monoclinic (a= 5.36, b= 4.69, c= 7.95) tellurium oxide was observed at pH: 12. Monoclinic Te_2O_5 was the dominant structure at pH: 11.50, but a tetragonal α-TeO_2 peak was also observed in the same sample. The structure of α-tellurium oxide and Te_2O_5 were produced γ-tellurium oxide (Orthorhombic, a= 12.03, b= 5.46, c= 5.60) at deposition pHs of 11 and 10. Blanchandin *et al.* studied tellurium oxide in detail[10]. They reported that the peaks of the α-TeO_2 peaks were determined at 2θ degrees at 25-26°, 30° and 37° and also, the peaks of the γ-TeO_2 peaks were observed at 27-29°, 36° and 38°. These results are in quite good agreement with the literature.

The structural parameters such as grain size (*D*) and dislocation density (δ), for all films were evaluated by the XRD patterns and are given in Table 1. The grain size of the thin films was calculated by XRD patterns using Debye Scherrer's formula[11]:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad \ldots (1)$$

where *D* is the grain size, λ is the X-ray wavelength used, β is the angular line width at half-maximum intensity in radians and θ is the Bragg's angle. The grain size and dislocation density of the films are calculated using the FWHM values of the

Table 1 —XRD data of ASTM values versus films

pH	ASTM data file	ASTM value	Observed value	Miller İndices
12	43-1047	31.554	31.332	Te_2O_5 (-201)
11.50	74-269	26.258	26.966	α-TeO_2 (110)
	43-1047	31.554	31.332	Te_2O_5 (-201)
11	74-1131	27.161	27.103	γ-TeO_2 (211)
10	74-1131	27.161	27.162	γ-TeO_2 (211)

peaks (Table 1) obtained through the Scherrer's method. The dislocation density (δ) given more information on the amount of defects in the films, and is given by the formula below[11]:

$$\delta = \frac{1}{D^2} \qquad \dots (2)$$

Higher δ values indicate lower crystallinity levels for the films and indicate the amount of defects in the structure. Films with larger D and smaller δ values indicate better crystallization of the films[11].

$$N = \frac{t}{D^3} \qquad \dots (3)$$

where N is the number of crystallites per unit area. The higher N value indicates abundance of crystallization.

Figure 2 shows the grain size (D), dislocation density (δ) and number of crystallites per unit area (N) values of tellurium oxide thin films at different pHs. The average grain size of the films did not change very much at pH: 10 and 11, but decreased and then increased at pH: 11.5 and 12. The dislocation density (δ) and the number of crystallites per unit area (N) values of tellurium oxide thin films had their highest value at the mixing phase of pH: 11.5. The average grain size with the lowest value was calculated at pH: 11.5.

The film thickness of the films is given in Fig. 3. The film thickness of the films was suitable at pH: 10 and 11. The film thickness at pH: 11.5 was the thinnest while the thickest film was obtained at pH: 12. It was shown that the number of crystallites of γ-TeO_2 grown at pH: 12 were greater than at pH: 11.5. Although the number of crystallites in the mixing phase at pH: 11.5 increased, the thickness of the film decreased. A thicker film than that obtained in this study was produced by researchers at 60-200 nm film thickness[12]. However they used the instrumental method as the thermal evaporation method. Although some methods can be used to produce thinner film than those obtained by chemical bath deposition, these methods are expensive and need special instruments.

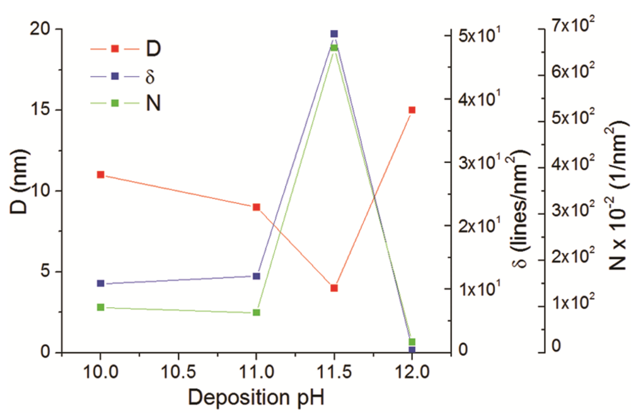

Fig. 2 —The grain size (D), dislocation density (δ) and the number of crystallites per unit area (N) values of tellurium oxide thin films at different pHs.

The transmittance (T) for tellurium oxide thin film can be calculated using reflectivity (R) and absorbance (A) spectra from the expression[11]:

$$T = (1-R)^2 e^{-A} \qquad \dots (4)$$

Transmission measurements given in Fig. 4 were performed at room temperature in the range of 300-1100 nm. The transmission changed markedly with different deposition pH. The highest transmission was observed at pH: 12 while the pH: 11.5 bath had the lowest transmission (at 550 nm wavelength). The reflectivity results were in contrast to the transmission results. The highest reflectivity

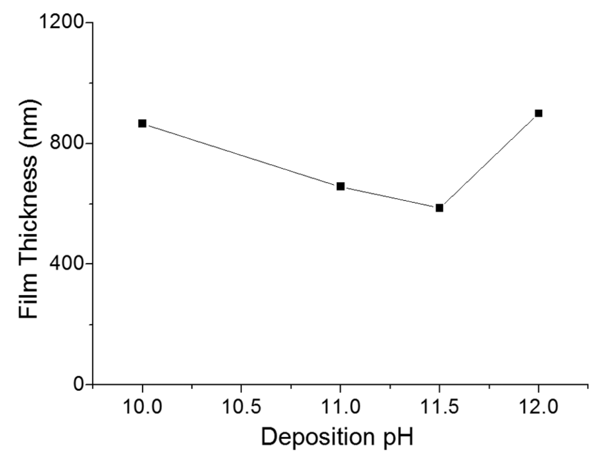

Fig. 3 — Film thickness of the tellurium oxide with different pHs.

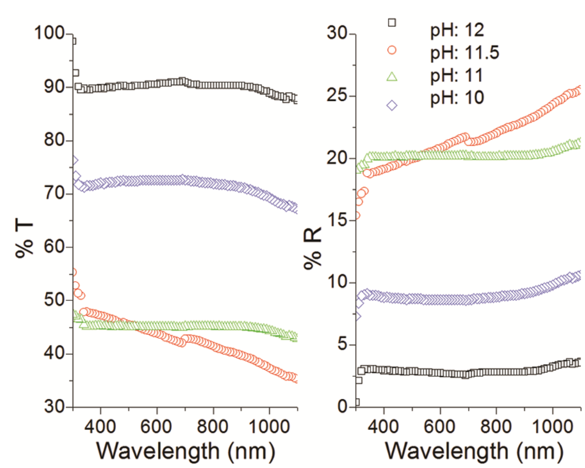

Fig. 4 — The transmittance (T) and reflectivity (R) of tellurium oxide thin films at different pHs.

was determined at pH: 11.5 while the lowest reflectivity was determined at pH: 12. The highest transmission was observed at pH: 12 because the best crystallization was obtained at this pH. Because of the mixing phase at pH: 11.5, the lowest transmission and lower reflectivity were observed at this pH. Al-Kuhaili *et. al.* also observed high transmission on tellurium oxide with 60-200 nm film thickness[13]. They produced their films by the thermal evaporation method.

The refractive index and extinction coefficient for films are given by the following formulas[11]:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad \dots (5)$$

$$k = \frac{\alpha\lambda}{4n} \quad \dots (6)$$

The refractive index and extinction coefficient are given in Fig. 5. The refractive index values were 1.40, 2.64, 2.63 and 1.83, at pH: 12, 11.50, 11, 10, respectively, in Fig. 5 (in 550 nm wavelength). Also the extinction coefficients behaved like the refractive index and at pH: 12, 11.50, 11, 10, were 0.003, 0.025, 0.025 and 0.010, respectively (in 550 nm wavelength). The highest refractive index value was 2.64 at pH: 11.50 and the highest extinction coefficient values were 0.0025 at pH: 11.50 and 11. Also, Al-Kuhaili *et al.* calculated the refractive index of tellurium oxide thin film at 2.0-2.3 and calculated *k* values[13] down to 0.020. These results are in agreement with this study.

The percentage of elemental ratio of tellurium in the structure at different pH is given in Fig. 6. The percentages of elemental ratio of tellurium in the structure were 74.35, 71.87, 77.18 and 78.41 % at pH: 12, 11.50, 11 and 10, respectively. These values are in agreement with the theoretical values of Te_2O_5 and TeO_2 which were 76.45 % and 79.95 %, respectively. The EDX results were in agreement with the XRD patterns and calculations.

Absorbance of the tellurium oxide thin film was calculated easily with Eq. (4). The absorbance of the tellurium oxide thin film is given in Fig. 7. The absorbance curves of tellurium oxide thin films were shown to have highest values at pH: 11.5 and 11. The reason for this is that the mixing phases were observed at pH: 11.5 as Te_2O_5 and TeO_2. Also, this result was in correlation with the number of crystallites per unit area, because the highest value was calculated in Fig. 2. It was probably the only dominated phase observed at pH: 11, but it contained both phases. Even though Al-Kuhaili *et al.* and

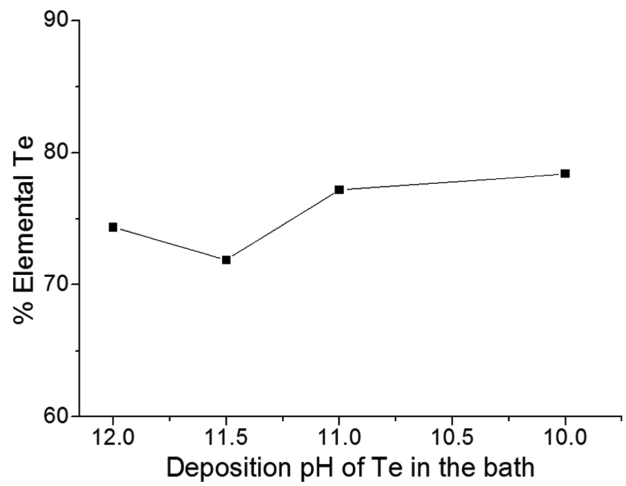

Fig. 6 — The percentage of elemental ratio of tellurium in the structure at different pHs.

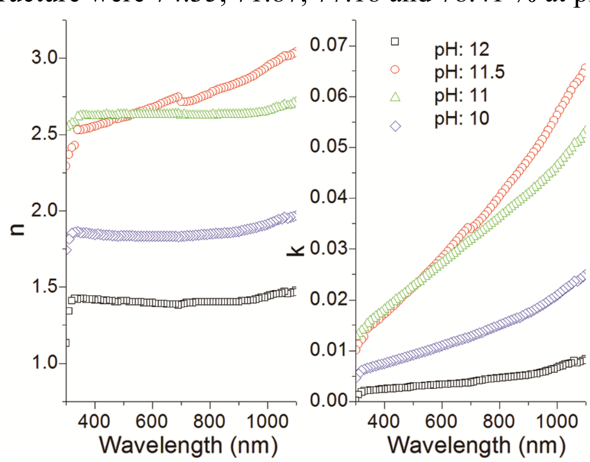

Fig. 5 ––The refractive index (*n*) and extinction coefficient (*k*) for tellurium oxide thin films at different pHs.

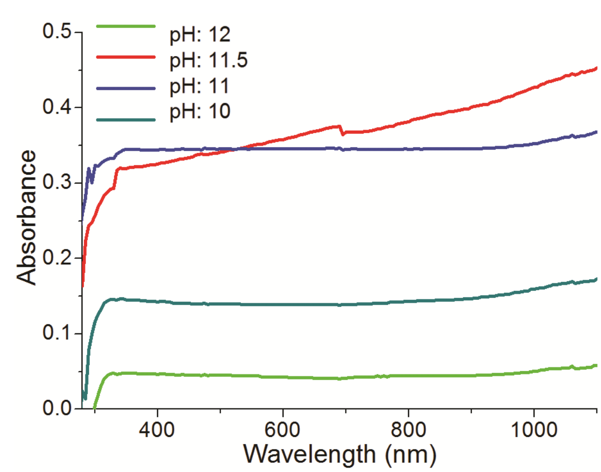

Fig. 7 — Absorbance of tellurium oxide thin film with different wavelengths.

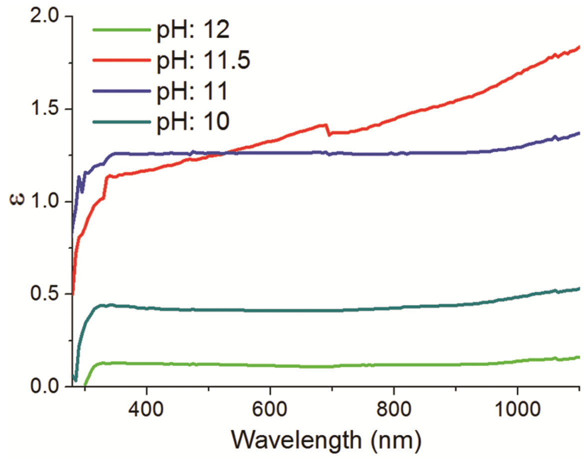

Fig. 8 — Dielectric constant (ε) of tellurium oxide thin film with different wavelength.

Lakshmınarayan *et al.* produced thinner films than those in this study, they also calculated the same values[12,13].

The dielectric constant (ε) can be calculated by following relation:

$$\varepsilon\varepsilon = \frac{4R}{1-R^2} - k^2 \quad \dots (7)$$

The dielectric constants of the tellurium oxide thin films in different pHs are given in Fig. 8. Higher dielectric constant values were observed at pH: 11.5 and 11, as absorbance curves. The optical dielectric constant is a marker for the attraction of grains to light. The grains of the number of crystalline per unit area and the mixing phases are more attracted than the tellurium oxide thin films produced at other pHs. These results are in agreement with the XRD results and absorbance curves. Until now, there has no study of the optical properties, such as reflectance, dielectric constant, etc., of tellurium oxide thin films.

4 Conclusions

Tellurium oxide has different phases: α-TeO_2, β-TeO_2, γ-TeO_2. However researchers have started working on the γ-TeO_2 structure for gamma radiation and for its properties, as mentioned in introduction. Therefore, γ-TeO_2 thin film was produced in this study and were investigated how to produce quality crystalline γ-TeO_2 thin films. Also, some of the properties of γ-TeO_2 thin films such as refractive index, transmission, reflectivity and structural properties were investigated in this study. The optimum parameters were determined with 10 ml $2.5\text{x}10^{-3}$ M tellurium tetrachloride, 10 mL 2.5×10^{-3} M potassium hydroxide and 2 mL hydrogen peroxide at pH: 10. This film may be useful in radioactive applications or other technologies such as for sensors, detectors and solar cells.

References

1 Phillips G W, Readshaw A K, Brown G O, Weiss R G, Guardala N A, Price J L, Mueller S C & Moscovitch M, *Appl Radiat Isot*, 50 (1999) 875.
2 Kariper İ A, *J Opt*, 47 (2018) 504.
3 Prakash G V, Rao D N & Bhatnagar A K, *Solid State Commun*, 119 (2001) 39.
4 Schlesinger T E, Toney J E, Yoon H, Lee E Y, Brunett B A, Franks L & James R B, *Mater Sci Eng*, 32 (2001) 103.
5 Shpotyuk O I, *Radiat Phys Chem*, 46 (1995) 1279.
6 El-Mallaway R A F, *Tellurite glasses handbook: Properties and data*, (CRC: Boca Raton, FL), 2002.
7 Dewan N, Sreenivas K & Gupta V, *J Crystal Growth*, 305 (2007) 237.
8 Champarnaud-Mesjard J C, Blanchandin S, Thomas P, Mirgorodsky A, Merle-Méjean T & Frit B, *J Phys Chem Solids*, 61 (2000) 1499.
9 Noguera O, Merle-Méjean T, Mirgorodsky A P, Smirnov M B, Thomas P & Champarnaud-Mesjard J C, *J Non-Cryst Solids*, 330 (2003) 50.
10 Blanchandin S, Thomas P, Marchet P, Champarnaud-Mesjard J C & Frit B, *J Mater Chem*, 9 (1999) 1785.
11 Pejova B, Grozdanov I & Tanusevski A, *Mater Chem Phys*, 83 (2004) 245.
12 Lakshminarayan N, Radhakrishnan M & Balasubraman C, *J Mater Sci*, 21 (1986) 246.
13 Al-Kuhaili M F, Durrani S M A, Khawaja E E & Shirokoff J, *J Phys D: Appl Phys*, 35 (2002) 910.