A STUDY ON OPTICAL AND STRUCTURAL PROPERTIES OF TELLURIUM OXIDE THIN FILMS FOR THE VARIATION OF SPUTTERING GAS RATIO

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1. Introduction

Tellurium oxide is one of the most attractive semiconductor materials, existing as both crystalline and amorphous phases. In particular, tellurium dioxide in crystalline form exists in two phase : paratellurite (tetragonal) and tellurite (orthorhombic). Tellurium dioxide has high acousto-optic figure of merit, chemical stability and mechanical durability. Thus, properties of tellurium oxide make it suitable for various application devices such as nonlinear optoelectronic, optical recording systems, optical devices (deflectors, modulators, tunable filters) and gas sensors [1-5].
Thin films of tellurium dioxide have been prepared by various methods such as RF Sputtering, sol-gel and thermal evaporation. The optical and structural characteristics of thin films of tellurium dioxide strongly depend on its chemical composition and parameters of growth (such as fabrication method, deposition rate, deposition temperature, annealing conditions and film thickness) [1-2].
There have been no reports on the structural and optical properties of thin films of tellurium oxide which were fabricated using RF reactive sputtering techniques from a composite tellurium dioxide target by the variation of sputtering gas ratio. In this work, we investigated various thin films of tellurium oxide which were deposited using RF reactive sputtering by various sputtering gas ratios. We report here study on the properties of thin films of tellurium oxide.

2. Experimental details

2.1. Preparation of thin films

Thin films of tellurium oxide were deposited by RF sputtering technique. The target material, tellurium dioxide(TeO_2), of purity 99.99%, was used to deposit thin films. The p-type Si (100) wafer and fused quartz were used as a substrate after cleaned by acetone, trichloroethylene, isopropyl alcohol, and DI-water.
Then, thin films of tellurium oxide were prepared by RF reactive sputtering from the composite TeO_2 target at room temperature on the p-type Si (100) wafer and fused quartz substrates. The RF reactive sputtering was conducted under power of 25 W and 50 W, base pressure of 4×10^{-8} Torr and working pressure of 5×10^{-3} Torr. In order to get various thin films of tellurium oxide, thin films were deposited in the presence of an oxygen(O_2) and an argon(Ar) gas. The thin films were prepared with varying Ar:O_2 pressures (Ar:O_2 = 50:0, 40:10, 25:25).
Annealing of deposited thin films carried out in an Ar atmosphere for 60 min from 300℃ to 500℃. Heat treatment process was progressed severally in order to prevent temperature side-effect.

2.2. Measurement of thin films

Thickness of thin films was observed by the scanning electron microscope (SEM). The structural phases of the thermal annealed films were evaluated by X-ray diffraction (XRD, X'pert PRO, Phillips)

and X-ray photoelectron spectroscopy (XPS, VGMULTILAB 2000).
The optical transmittance spectrum (T_{OP}) of the quartz substrate was measured in the wavelength (λ) range of 200-800 nm using a UV-vis spectrophotometer (Cary-300, VARIAN).

3. Results and Discussion

Fig. 1 showed physical appearance of the films. The as-deposited films had various color such as black, light yellow and light blue, as increasing oxygen contents in the sputtering gas. In addition, the annealed films varied various color (such as light pink, light green and light yellow), as increasing annealing temperature. It could be because of variations in the stoichiometry of the deposited films [4].

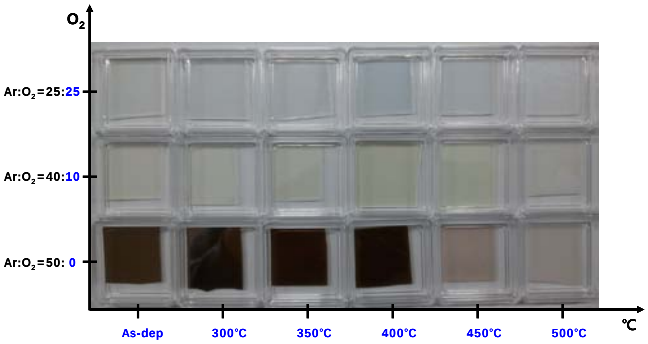


Fig. 1. The images of physical appearance of thin films according to increasing oxygen contents in the sputtering gas

Thickness of the films with gas mixture content of $Ar:O_2$ ($Ar:O_2$ = 50:0, 40:10, 25:25) were indicated in the Fig. 2 and Fig. 3. Fig. 2 and Fig. 3 show the scanning electron microscope (SEM) image which presents thickness of the sputtering power of 25 W and 50 W, respectively. We confirmed that the thickness of films is under the 5% error range. The films which deposited by power of 25 W were evaluated for X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). And the films which deposited by power of 50 W were evaluated for UV-visible spectrophotometer.

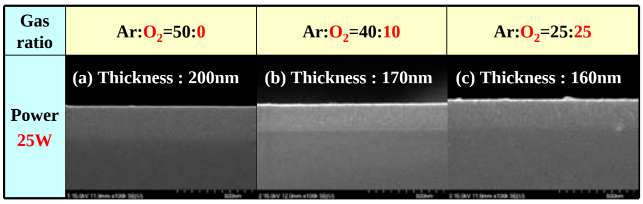


Fig. 2. SEM images of tellurium oxide thin films deposited by the sputtering power of 25 W :
(a) $Ar:O_2$=50:0, (b) $Ar:O_2$=40:10 (c) $Ar:O_2$=25:25

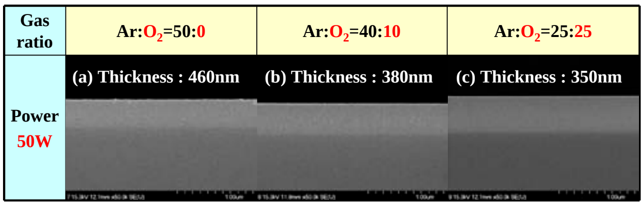
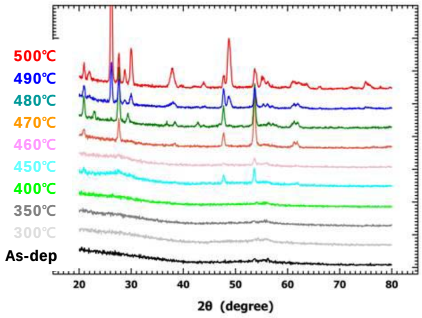


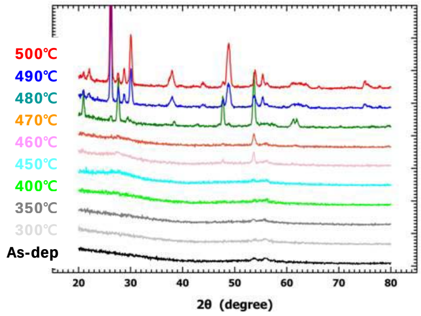
Fig. 3. SEM images of tellurium oxide thin films deposited by the sputtering power of 50 W :
(a) $Ar:O_2$=50:0, (b) $Ar:O_2$=40:10 (c) $Ar:O_2$=25:25

3.1. Structural properties

XRD analysis of thin films on p-type Si (100) substrates was carried out at different annealing temperature and $Ar:O_2$ gas pressures. Fig. 4 (a) ~ (b) present XRD pattern of thin films with increasing annealing temperature and increasing oxygen contents in the sputtering gas. XRD peaks of thin films which were deposited with only Ar gas remain amorphous at the as-deposition state. After annealing, various peaks (such as hexagonal, tetragonal and orthorhombic) were observed. Fig. 4 (a) shows XRD peaks of thin films which were deposited with gas mixture content of $Ar:O_2$ = 40:10. As-deposited film was amorphous and remained amorphous even after annealing treatment up to 400℃, as indicated in Fig. 4 (a). The XRD peaks of 450℃ and 460℃ had tetragonal crystal structure. And the XRD peaks of annealed the film after the annealing temperature of 470℃ had tetragonal and orthorhombic crystal structure. In addition, Fig. 4 (b) shows XRD peaks of thin films which were deposited with gas mixture content of $Ar:O_2$ = 25:25. The annealed film up to 450℃ did not induce crystalline. The tetragonal crystal structure appeared at the annealing temperature of 460℃ and 470℃. And more than the annealing temperature of 480℃ had tetragonal and orthorhombic crystal structure.



(a)



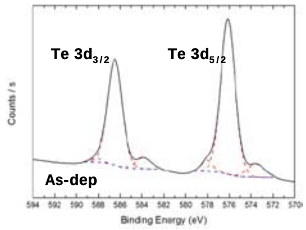
(b)

Fig. 4. XRD pattern of thin films : (a) $Ar:O_2$=40:10 (b) $Ar:O_2$=25:25

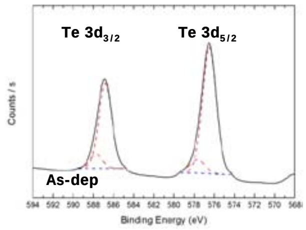
The XPS spectrum of Te 3d and O 1s peak was obtained. In order to confirm binding energy of tellurium oxide, the XPS spectra of Te $3d_{5/2}$ and O 1s used (Fig. 5). The value of binding energy was presented by $Ar:O_2$ ratio, as shown in the Table 1. In case of $Ar:O_2$ = 50:0 ratio, the peak at 530.35eV corresponding to O 1s element, whereas the peak corresponding to Te $3d_{5/2}$ was measured at 576.15eV. So, Te-Te bond energy was observed at 574.65eV. The presence of metallic Te and tellurium oxide detected by XRD was confirmed by XPS spectrum of Te $3d_{5/2}$. In addition, in case of $Ar:O_2$ = 40:10 and $Ar:O_2$ = 25:25 ratio, because no peak other than O and Te elements was observed in the XPS spectrum, composition of thin films were confirmed by tellurium oxide [2,4].

Table 1. XPS result of thin films

type	O 1s [eV]	Te $3d_{5/2}$ [eV]
$Ar:O_2$=50:0	530.35	576.15
$Ar:O_2$=40:10	530.75	576.5
$Ar:O_2$=25:25	530.8	576.55



(a)



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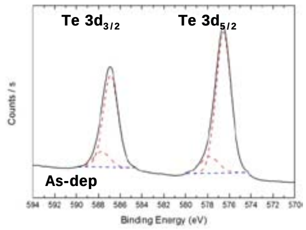
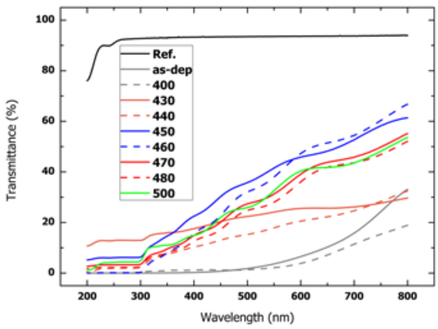


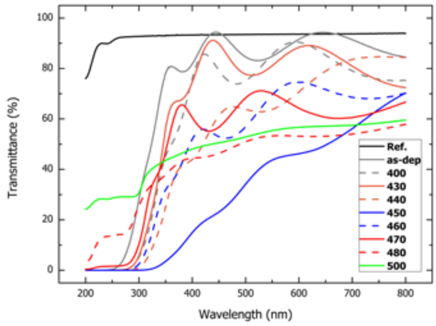
(c)

Fig. 5. XPS spectrum of Te 3d of thin films : (a) $Ar:O_2$=50:0, (b) $Ar:O_2$=40:10 (c) $Ar:O_2$=25:25

Fig. 6 show the transmittance spectra of as-deposited and annealed thin films. In case of $Ar:O_2$ = 40:10 and $Ar:O_2$ = 25:25, as-deposited thin films presented high transmittance and transmittance of post-annealed thin films was reduced. In case of $Ar:O_2$ = 50:0 ratio, due to the presence of metallic Te, transmittance of the thin film was lower than other films. In all cases transmittance spectra of thin films divided into two regions : weak and strong absorption. [1,8].



(a)



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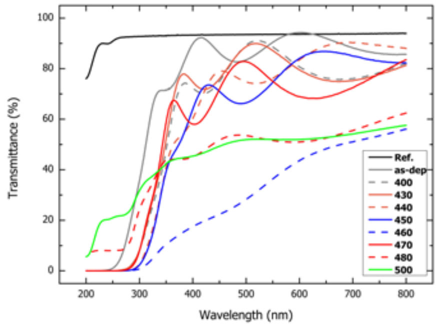

(c)

Fig. 6. Transmittance spectra of thin films : (a) $Ar:O_2$=50:0, (b) $Ar:O_2$=40:10 (c) $Ar:O_2$=25:25

4 Conclusion

This study was demonstrated optical and structural properties of TeO_2 thin films using RF reactive sputtering technique from the tellurium dioxide (TeO_2) target. Moreover, thin films of tellurium oxide were annealed in an Ar atmosphere for 1 hour. All as-deposited films were amorphous. By increasing annealing temperature, the XRD result of deposited thin films with gas mixture content of $Ar:O_2$ ($Ar:O_2$ = 40:10, 25:25) had crystal structures such as tetragonal and orthorhombic.

The XPS peak was measured, too. The thin films with $Ar:O_2$ ($Ar:O_2$ = 40:10, 25:25) ratio showed binding energy of tellurium oxide, respectively. However, due to the presence of metallic Te and tellurium oxide, Te-Te and Te-O bond simultaneously were confirmed at the thin film with only Ar gas.

In case of $Ar:O_2$ = 40:10 and $Ar:O_2$ = 25:25, as-deposited thin films presented high transmittance and transmittance of post-annealed thin films was reduced. In case of $Ar:O_2$ = 50:0 ratio, transmittance of the thin film was lower than other films. Calculation of energy band gap (E_{OP}) is presently in progress. In addition, in order to get attractive properties of tellurium oxide thin films, additional studies are in progress.

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