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Electrical and optical properties of tantalum oxide thin films prepared by reactive magnetron sputtering

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ABSTRACT

Tantalum oxide thin films were prepared by using reactive dc magnetron sputtering in the mixed atmosphere of Ar and O_2 with various flow ratios. The structure and O/Ta atom ratio of the thin films were analyzed by X-ray diffraction and X-ray photoelectron spectroscopy (XPS). The optical and dielectric properties of the Ta_2O_5 thin films were investigated by using ultraviolet–visible spectra, spectral ellipsometry and dielectric spectra. The results reveal that the structure of the samples changes from the amorphous phase to the β-Ta_2O_5 phase after annealing at 900 °C. The XPS analysis showed that the atomic ratio of O and Ta atom is a stoichiometric ratio of 2.50 for the sample deposited at Ar:O_2 = 4:1. The refractive index of the thin films is 2.11 within the wavelength range 300–1000 nm. The dielectric constants and loss tangents of the Ta_2O_5 thin films decrease with the increase of measurement frequency. The leakage current density of the Ta_2O_5 thin films decreases and the breakdown strength increases with the increase of Ar:O_2 flow ratios during deposition.

1. Introduction

Ta_2O_5 thin film is wildly applied for optoelectronic and microelectronic applications. In optical and optoelectronic applications, Ta_2O_5 thin film is used as a high index and low loss materials for optical waveguides interference filters, high-reflective thin films mirrors for solar cells, charge coupled devices (CCDs), high power laser equipments and electroluminescent devices [1–5]. In microelectronic applications, Ta_2O_5 thin film is used in high-density dynamic-random-access memories (DRAMs) as well as in metal–oxide–semiconductor field-effect transistors (MOSFETs) due to its high dielectric constant, high chemical, thermal stability, low leakage-current density and being compatible with the microelectronic processing technology [6,7]. Deposition techniques such as thermal evaporation [8], rf and dc reactive magnetron sputtering [9,10], electron beam evaporation [11], pulsed laser deposition [12], atomic layer deposition [13], and metal–organic chemical vapor deposition [14] are employed for deposition of Ta_2O_5 thin films. Among these techniques, reactive magnetron sputtering has the advantage in the preparation of uniform films on large area substrates by sputtering of metallic tantalum target in the presence of reactive gas of oxygen. The physical properties of the magnetron sputtered thin films mainly depend on the process parameters such as oxygen partial pressure, substrate temperature, sputtering power and the distance between the target and substrate. In this investigation, an attempt was made in the preparation of Ta_2O_5 thin films by rf reactive magnetron sputtering technique at various Ar:O_2 flow ratios. The influence of Ar:O_2 flow ratios on the chemical binding configuration, structure, dielectric and optical properties were studied systematically. The optical constants of tantalum oxide thin films at the wavelength range of 250–1000 nm were first determined and reported. The main factors affecting the value of the refractive index n and the extinction coefficient k of the thin films were discussed. The frequency dependence of the dielectric constant and the loss tangent of tantalum peroxide films were also discussed.

2. Experimental method

The tantalum oxide thin films were deposited by reactive dc magnetron sputtering at room temperature under an Ar/O_2 ambient. The target was a 75 mm diameter Ta metal plate placed over one of the cathode. Si and high-purity quartz wafers were used as substrates. The chamber was pumped down to 6×10^{-4} Pa and backfilled with the sputtering gas to a pressure of 1.6 Pa. The mixtures of Ar and O_2 with various flow ratios of 1:1, 2:1, 3:1 and 4:1 were used. A sputtering voltage of 0.36 kV and a sputtering current of 0.16 A were applied to the target. The sputtering time was 60 min. The thicknesses of thin films determined by using an Ambios XP-2 α-step meter are 57.8, 94.3, 171.8 and 255.0 nm, corresponding to samples deposited at Ar:O_2 flow ratios of 1:1, 2:1, 3:1 and 4:1, respectively.

The thin films used for X-ray diffraction (XRD), scanning electron microscopy (SEM, S-3400 N), X-ray photoelectron spectroscopy (XPS) and SE measurements were deposited onto Si(1 0 0) substrates. The thin films used for measurement of the optical absorption and dielectric constant were deposited onto 20 mm × 10 mm quartz substrates. The structure of the thin films was analyzed with D/MAX2200

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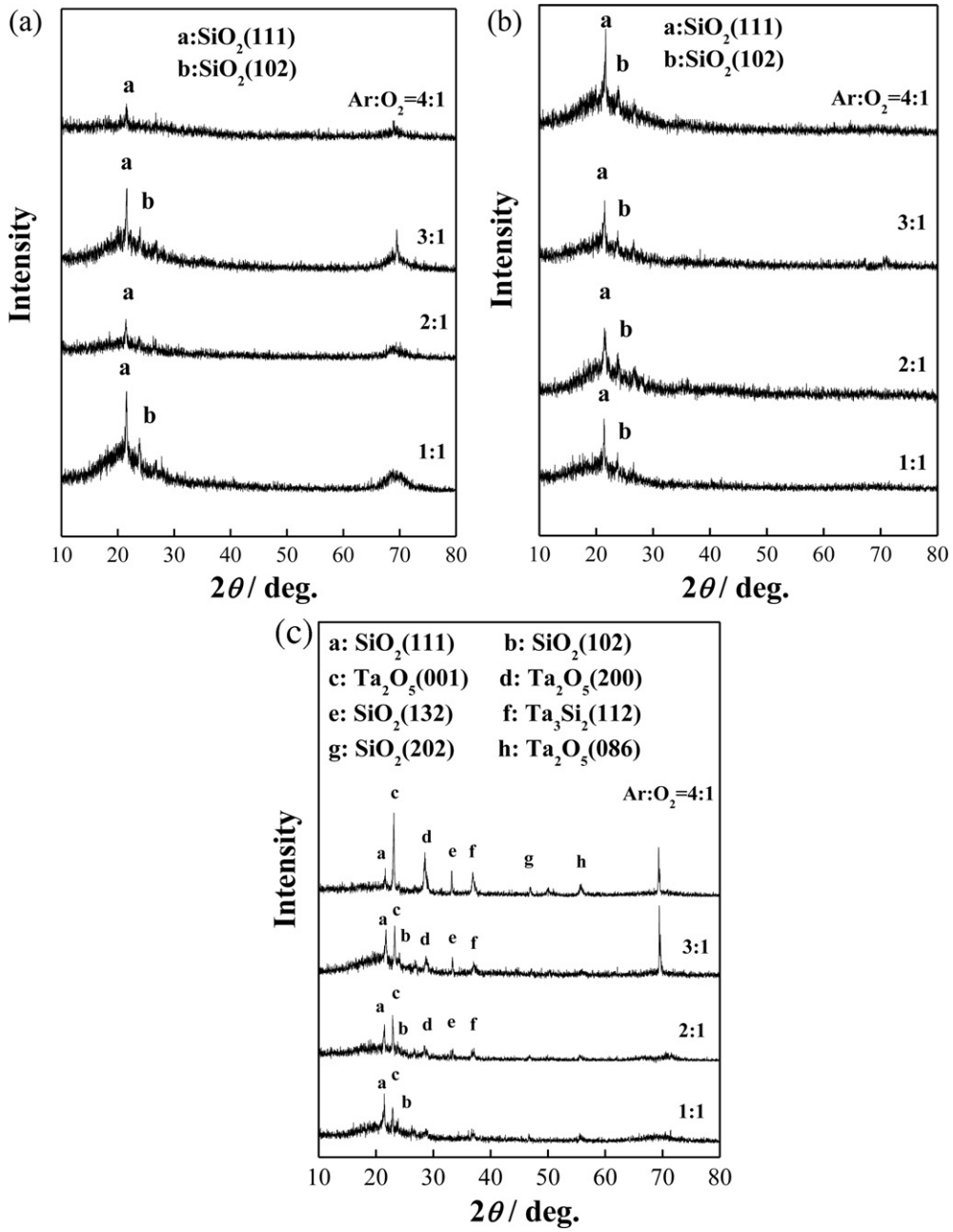

Fig. 1. XRD patterns of as-grown and annealed films deposited at various $Ar:O_2$ flow ratios as indicated: (a) as-grown films; (b) films annealed at 400 °C for 30 min; and (c) films annealed at 900 °C for 30 min.

VPC XRD before and after annealing at 400 and 900 °C for 30 min in atmosphere. The ratio of the oxygen to tantalum content in the films was calculated from XPS high resolution spectra obtained by an ESCALAB 250 X-ray photoelectron spectrometer. The ellipsometric spectra of the films, namely, the ellipsometric parameters ψ and Δ, was measured in the 250–1000 nm wavelength range and at an incident angle of 70° by using a Woollam M-2000U automatic ellipsometer. The measured ellipsometric spectra of two samples was calculated by using a three-layer model (Si substrate/Ta_2O_5/rough surface) and an optimization algorithm [15]. The optical constants of the thin films in the 250–1000 nm wavelength range were obtained. Optical absorption measurement was carried out by means of a double-beam UV–visible spectrometer in the 200–700 nm wavelength range in comparison with an uncoated quartz substrate in the reference beam to eliminate contributions from the substrate. The Ta/Ta_2O_5/Ta capacitors were made on quartz substrates. Ta electrodes were deposited on the top by dc sputtering and circular electrodes with an area of 1.57×10^{-2} cm^2 were formed during sputtering by using the shadow mask technique. The frequency dependence of the dielectric constant and the loss tangent for samples deposited at various $Ar:O_2$ flow ratios were measured by an HP 4192 A LCR meter. The current–voltage characteristics of samples were measured by using Keithley 6487 pA meter.

3. Results and discussion

3.1. Structure and stoichiometry

XRD patterns for as-deposited and annealed at 400 °C and 900 °C samples grown at various $Ar:O_2$ flow ratios were measured and typical results were shown for comparison in Fig. 1. The XRD results indicate that the as-deposited films and those annealed at 400 °C are amorphous. However, for the sample annealed at 900 °C, crystallization is observed, as evidenced by two peaks around 23.1° and 28.5°, corresponding to the (0 0 1) and (2 0 0) peak of β-Ta_2O_5 thin films. Dimitrova et al. [16] observed amorphous to crystalline phase transition when rf magnetron sputtered samples were annealed at the annealing temperatures of 600–850 °C. Recent report also described that the minimum required temperature to obtain crystalline Ta_2O_5 layer on Si substrate should be 700 °C [17]. The

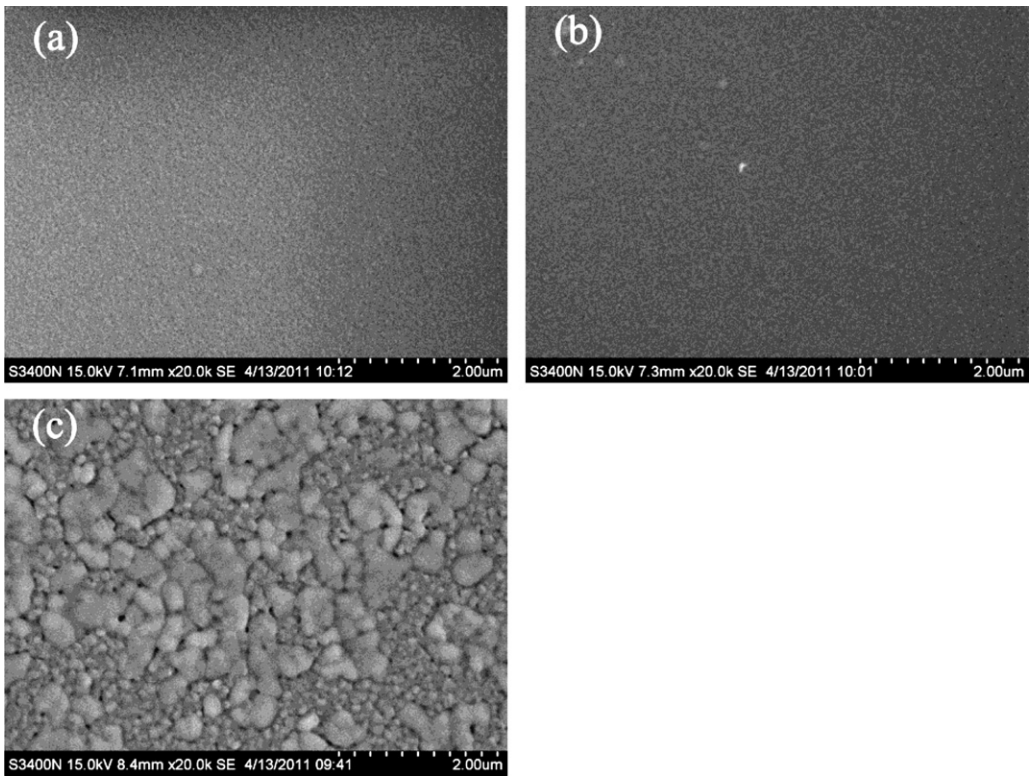

Fig. 2. SEM image of tantalum oxide films prepared at Ar:O_2 flow ratio of 4:1. (a) As-deposited films; (b) Annealed at 400 °C for 30 min; (c) annealed at 900 °C for 30 min.

structure evolution of the sample as a function of Ar:O_2 flow ratio was shown in Fig. 1. It can be seen that more Ar in the Ar:O_2 ambient is favorable for crystallization and growth of Ta_2O_5 thin films. In addition, the (1 1 1) and (1 0 2) peaks of SiO_2 can be clearly seen for the as-deposited and annealed thin films. The SiO_2 interfacial layer always arises due to the reaction between Ta_2O_5 and the silicon substrate during deposition of the Ta_2O_5 thin films. The thickness of the SiO_2 interfacial layer varies with the deposition process and post-deposition annealing parameters.

Fig. 2 shows SEM images of the as-prepared and annealed at 400 °C and 900 °C thin films deposited at an Ar:O_2 flow ratio of 4:1. It can be seen from Fig. 2 that relatively smooth surface was observed in the as-deposited and annealed at 400 °C sample (Fig. 2a and b). The smooth surface characterization is due to the amorphous nature of these thin films. Such an amorphous phase with smooth surface was also obtained by Huang [18] in liquid phase deposited tantalum oxide thin films. As the annealing temperature increases, the thin films exhibit polycrystalline nature (Fig. 2c), which is consistent with the XRD data well.

The ratio of the oxygen to tantalum content in the thin films was studied by XPS analysis. Fig. 3(a) shows a typical XPS spectrum of thin films deposited at an Ar:O_2 flow ratio of 2:1. As can be seen, the Ta 4f, Ta 4d, Ta 4p1, Ta 4p3 and O1s peaks are easily identified. C 1s peak is also observed. The peaks existing at 27.8 and 29.7 eV come from the Ta $4f_{7/2}$ and Ta $4f_{5/2}$, respectively. The peaks of 27.8 eV is corresponds to +5 oxidation state of Ta. The core level binding energy of Ta$4f_{7/2}$ in elemental tantalum is 22.5 eV [19]. A chemical shift of 5.3 eV was observed in the Ta_2O_5 thin films sample. Khanuja et al. [19] also achieved a chemical shift of 4.9 eV in films prepared by oxide. The O/Ta atomic ratio of the thin films can be calculated from the ratio of the integrated intensities of the O 1s to Ta 4f lines, corrected by using the sensitive factors $S_O = 0.66$ and $S_{Ta} = 2.40$. A closer look at the XPS spectra suggests that both the Ta 4f and O 1s lines can be deconvoluted into Gaussian components. Examples of such a deconvolution are shown in Fig. 3(b) and (c). There are two characteristic Gaussian peaks in the Ta 4f spectra and two in the O 1s spectra. The binding energy and the atomic ratio O:Ta calculated from XPS data at different Ar:O_2 flow ratio are listed in Table 1. The only stoichiometric ratio 2.5:1 is achieved for the sample deposited at a Ar:O_2 flow ratio of 4:1 from the list of the atomic ratios. These results indicate that an appropriate amount of Ar in the Ar:O_2 ambient is favorable for forming stoichiometric Ta_2O_5. Our results were compared to those reported by Wu et al. [20], in which the Ta_2O_5 thin films were prepared by using RF magnetron sputtering with ceramic Ta_2O_5 target in a pure O_2 atmosphere at different substrate temperatures. The binding energy and the atomic ratio O:Ta calculated from XPS data are listed in Table 2. It has been reported [18]

Table 1
Binding energy and chemical atomic ratio O:Ta calculated from XPS data at different Ar:O_2 flow ratios.

Ar:O_2 flow ratios	Ta $4f_{7/2}$ (eV)	Ta $4f_{5/2}$	O1s (eV)	O:Ta
1:1	25.7	27.5	530.5	2.71:1
2:1	25.4	27.2	530.4	2.70:1
3:1	27.8	29.6	530.1	2.60:1
4:1	27.8	29.7	530.3	2.50:1

Table 2
Binding energy and chemical atomic ratio O:Ta calculated from XPS data at different substrate temperatures by Wu et al. [20].

Substrate temperature (°C)	Ta 4f7/2 (eV)	O 1s (eV)	O:Ta
No-heating	24.7	529.5	2.19:1
100	25.3	530.1	2.14:1
200	25.5	529.8	2.09:1
300	25.3	529.3	2.23:1
400	26.8	531.7	2.50:1

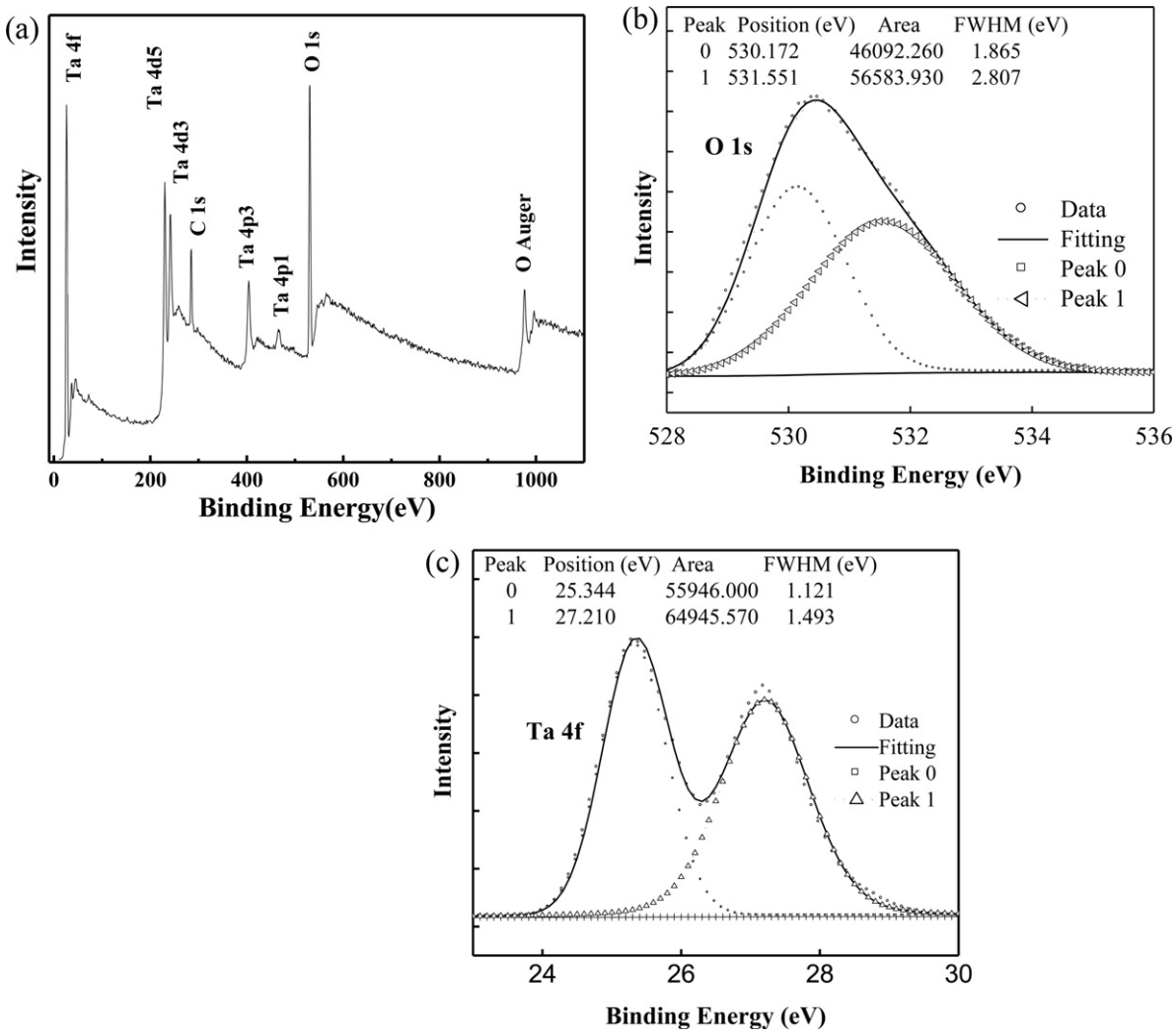

Fig. 3. (a) Typical XPS spectrum of films deposited at an Ar:O_2 flow ratio of 2:1. Typical deconvolution of (b) the XPS O 1s and (c) the Ta 4f spectrum into two Gaussian components for films deposited at Ar:O_2 = 2:1.

that a comparatively oxidized stoichiometric Ta_2O_5 thin film has superior dielectric property to the non-stoichiometric one.

3.2. Optical properties of tantalum oxide

SE is a non-destructive and powerful characterization technique which is available for quantitatively measuring the thickness and optical constants of thin films. The ellipsometric parameters tan ψ and cos Δ were measured as a function of photon wavelength in the range of 250–1000 nm. The measured and calculated ellipsometric spectra are shown in Fig. 4(a). A three-layer structure model (Si-substrate/Ta_2O_5/rough surface) was used to simulate the measured spectra, in which the thickness, refractive index (n) and extinction coefficient (k) were regarded as the fitting parameters. Remarkably good fits are obtained in the whole wavelength range. The thickness of the thin films determined from the simulated SE is in agreement with that measured by the α-step meter. Values of n and k of the thin films determined from the simulated SE are shown in Fig. 4(b). The curves of n and k values as a function of photon wavelength were determined and reported. The refractive indices are about 2.11 and 2.06 in the wavelength range of 500–1000 nm for the thin films deposited at Ar:O_2 = 1:1 and 2:1, which are very close to the value for bulk Ta_2O_5 of 2.2. The variation of k is not significant in the long-wavelength range. The discrepancies of n values for different samples may be attributed to their rough surface. According to the theory in Ref. [21], the existence of voids decreases n. Voids and other structural disorder defects can also affect the other optical properties of the thin films.

Fig. 5 shows transmittance spectra of the thin films deposited with various Ar:O_2 flow ratios. An optical transmittance higher than 80% in the visible region of the spectrum is obtained for all samples. A sharp absorption edge was observed at about 250–300 nm. The optical absorption edge of the thin films shifts towards the lower wavelength side and increases with the increase of Ar:O_2 flow ratio. The optical band gaps of the thin films may be determined from the strong absorption edge at the wavelength range of 250–300 nm. According to the formula $E = hc/\lambda$, the optical band gaps of the films are calculated to be 4.97, 4.81, 4.68 and 4.47 eV for thin films deposited at the Ar:O_2 flow ratios of 1:1, 2:1, 3:1 and 4:1, respectively. The optical band gaps are very close to the value reported in Ref. [22]. The strong absorption edge in the wavelength range 250–300 nm is in agreement with the extinction coefficient k decreasing in slope in the same wavelength range.

3.3. Dielectric spectra of Ta_2O_5 thin films

For electrical measurement, Ta/Ta_2O_5/Ta capacitors with dc sputtered Ta electrodes were fabricated on a quartz sub-

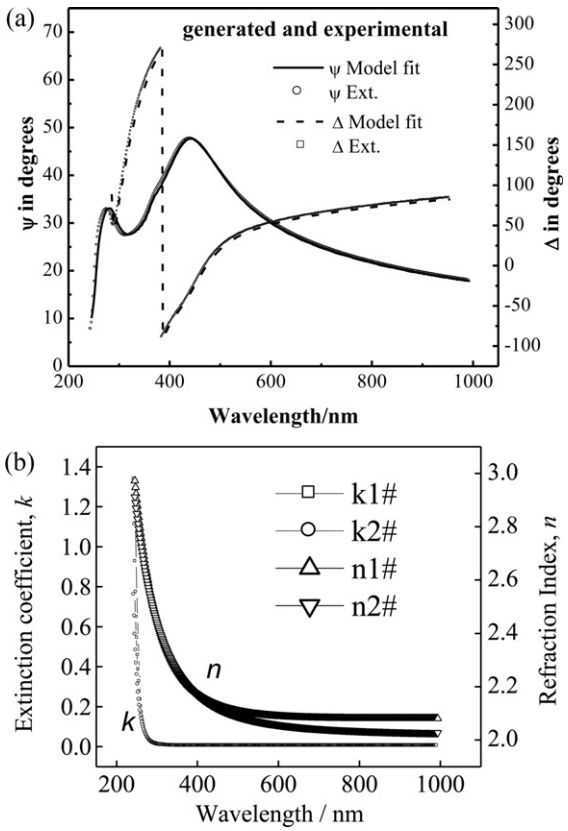

Fig. 4. SE and optical parameters determined from simulation of ellipsometric spectra: (a) measured and simulated ellipsometric spectra using a three-layer model; (b) n and k of Ta_2O_5 thin films deposited at $Ar:O_2$ = 1:1 and 2:1.

strate. Capacitance–frequency (C–f) and loss tangent–frequency ($\tan\delta$–f) characteristics were measured in the frequency range 500 Hz–13 MHz using an HP 4192 A LCR meter. The dielectric constant is calculated according to $C = \varepsilon\varepsilon_0 A/d$ with the known thickness and area. The experimental results obtained at a bias voltage value of 1 V at the measurement range of 500 Hz–13 MHz are presented in Fig. 6. It is seen that the dielectric properties of the tantalum oxide films strongly depend on the frequency. The dielectric constant and loss tangent rapidly decrease with increasing frequency at the lower frequency range; the capacitance and loss tangent do

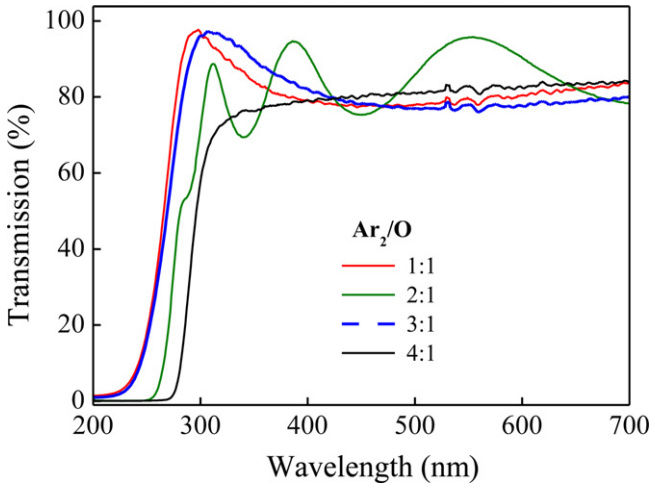

Fig. 5. Transmittance spectra of Ta_2O_5 thin films deposited at various $Ar:O_2$ flow ratios as indicated.

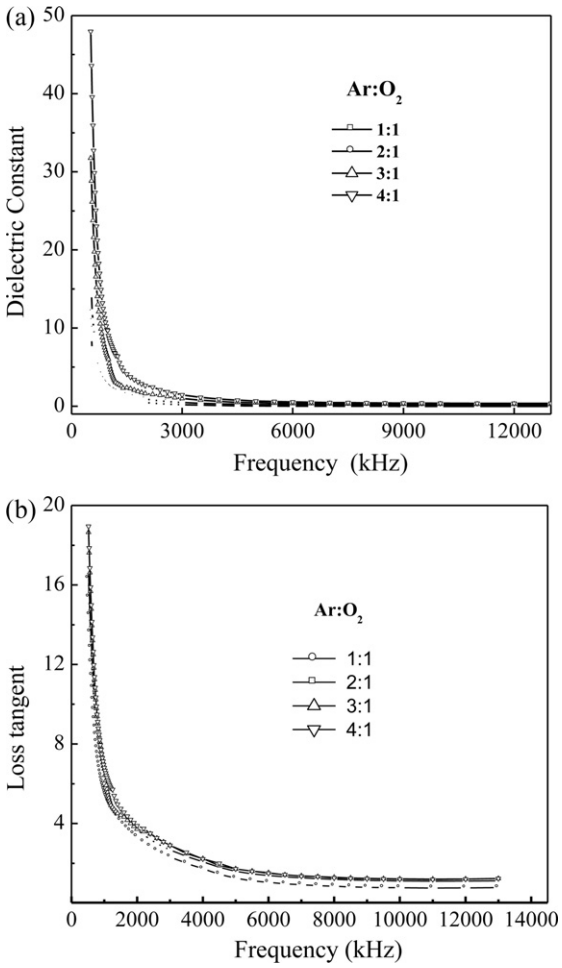

Fig. 6. Frequency dependence of the dielectric constant and the loss tangent for Ta_2O_5 films deposited at various $Ar:O_2$ flow ratios as indicated: (a) ε–f curve and (b) $\tan\delta$–f curve.

not change with frequency at the higher frequency range. Typical values of the dielectric constant are about 8.8, 14.6, 31.7 and 47.9 at a frequency of 500 Hz, and 3.9, 6.1, 18.2 and 18.7 at a frequency of 1 MHz for the thin films deposited with the $Ar:O_2$ flow ratios of 1:1, 2:1, 3:1 and 4:1, respectively. Typical values of the loss tangent are about 6.8, 5.8, 6.2 and 6.7 at a frequency of 1 MHz for the thin films deposited with the $Ar:O_2$ flow ratios of 1:1, 2:1, 3:1 and 4:1, respectively. Typical current–voltage characteristics of $Ta/Ta_2O_5/Ta$ capacitors using Keithley 6487 pA meter are shown in Fig. 7. The leakage current density decreases with the increasing of the $Ar:O_2$ flow ratios. For thin films deposited at the $Ar:O_2$ flow ratios of 4:1, the leakage current density decreases to 1×10^{-6} A cm^{-2}. The breakdown strength of the Ta_2O_5 thin films at a leakage current density of 1×10^{-5} A cm^{-2} was increased by increasing the $Ar:O_2$ flow ratios as shown in Fig. 7. The thin films deposited at the $Ar:O_2$ flow ratios of 4:1 possesses a high breakdown strength value of 0.54 MV/cm.

Our results were compared with tantalum oxide films prepared with other methods listed in Table 3. The optical and electrical properties of Ta_2O_5 thin films prepared by the reactive magnetron sputtering are similar with those prepared with other methods. However, the reactive magnetron sputtering has an obvious advantage, which is the preparation of uniform thin films on large area substrates by sputtering of metallic tantalum target in the presence of reactive gas of oxygen.

Table 3
Our results compared with those obtained by other deposition techniques.

Deposition techniques	Breakdown strength (MV/cm)	Leakage current density (A/cm^2)	Optical band gaps (eV)	Refractive index (550 nm)	O:T atomic ratio	Average transmittance (%)	Dielectric constant (1 MHz)
rf magnetron sputtering	0.54	1×10^{-6}	4.47	2.11	2.5:1	80	18.7
rf magnetron sputtering [9]	4.8	6.1×10^{-9}	–	2.10	–	–	–
Pulsed laser deposition [12]	–	–	4.18	2.22	2.5:1	82	23.9
Thermal oxidation [8]	0.7	7×10^{-10}	–	2.10	–	–	19.8
dc magnetron sputtering [10]	1	5.9×10^{-11}	4.50	2.14	–	–	27
Electron beam deposition [11]	–	–	4.56	2.07	–	80	–
Atomic layer deposition [13]	1	1×10^{-8}	4.20	2.13	2.5:1	90	22–25

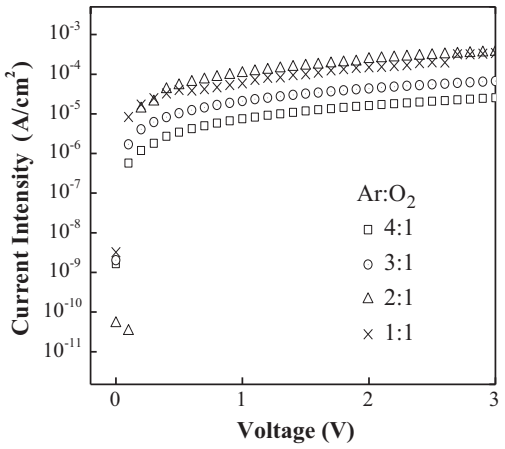

Fig. 7. *J–V* curves of films deposited at various Ar:O_2 flow ratio as indicated.

4. Conclusions

Effects of the Ar:O_2 flow ratio on the growth rate, structure, stoichiometry, optical constant and dielectric properties of tantalum oxide thin films have been studied. Results indicate that a larger amount of Ar in the Ar:O_2 ambient is favorable for the crystallization, growth and formation of stoichiometric Ta_2O_5. The ellipsometric spectra of the Ta_2O_5 thin films have been measured and simulated by using a multilayer structure model. It is shown that the SE technique is a valid method for determining the thickness and optical constants of the sample. The optical constants of tantalum oxide in the wavelength range 250–1000 nm have been determined and reported for the first time. The main factors affecting the values of n and k have also been discussed. The leakage current density of the Ta_2O_5 thin films decreases and the breakdown strength increases with the increasing of Ar:O_2 flow ratios.

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