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Growth and electrical characteristics of rf magnetron sputtered Ta_2O_5 films on Si

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Rf magnetron sputter technique was used for deposition of Ta_2O_5 films on silicon (111) and quartz substrates by sputtering of tantalum target under various oxygen partial pressures in the range $5x10^{-5}$ – $5x10^{-4}$ mbar and at a substrate temperature of 673 K. The effect of oxygen partial pressure on the chemical binding configuration, crystal structure, electrical and optical properties was investigated. The X-ray photoelectron spectra revealed that the films formed at oxygen partial pressure $\geq$ $1x10^{-4}$ mbar were stoichiometric. The dielectric constant increased from 17 to 22 by increasing the oxygen partial pressure from $5x10^{-5}$ to $5x10^{-4}$ mbar due to the improvement in the crystallinity and packing density of the films. The single phase films formed at an oxygen partial pressure of $1x10^{-4}$ mbar showed low leakage current density of $4x10^{-9}$ A/cm^2. The optical band gap of the films increased from 4.36 to 4.44 eV with the increase of oxygen partial pressure.

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1. Introduction

Tantalum oxide (Ta_2O_5) is a potential material alternate to the conventional insulators like silicon dioxide and silicon nitride for applications as capacitors in dynamic random access memory devices apart from the antireflection coatings for silicon solar cells, optical wave guides and protective coatings [1]. Several attempts were made to use Ta_2O_5 films as storage capacitors for high density random access memories [2]. But some of the problems remain be overcome before required reliability can be provided in the high density DRAM applications. One of them is the crystallinity of the Ta_2O_5 films highly influence the breakdown strength [3]. Different thin film preparation methods such as electron beam evaporation [4], pulsed laser deposition [5], chemical vapor deposition [6], ion beam evaporation [7] and dc / rf magnetron sputtering [8 -12] were employed for deposition of tantalum oxide films. The physical properties of the deposited films depend on the technique employed and the process parameters maintained during the formation. In our earlier investigation, the influence of postdeposition annealing in air on the structural and optical properties of rf magnetron sputtered Ta_2O_5 films was reported [13]. In the present investigation, an attempt is made to prepare Ta_2O_5 films by rf magnetron sputtering under different oxygen partial pressures and studied the influence of oxygen partial pressure on the chemical binding configuration, structure, electrical, dielectric and optical properties.

2. Experimental

Tantalum oxide films were formed on single crystal silicon (111) and quartz substrates using rf magnetron sputtering method. Pure tantalum target of 50 mm diameter and 1 mm thick was used as a sputter target. The ultimate pressure of 2×10^{-6} mbar was obtained in the sputter chamber using the combination of diffusion pump and rotary pump. Pure oxygen and argon were used as reactive and sputtering gases respectively. These gases were admitted into the sputter chamber through the fine controlled needle valves and their flow rates were monitored individually using Tylan mass flow controllers. The details of the Ta_2O_5 film deposition were given in our earlier paper [13]. Ta_2O_5 films were deposited by sputtering of tantalum target at a substrate temperature 673 K, under various oxygen partial pressures in the range 5×10^{-5} - 5×10^{-4} mbar and at a sputtering pressure of 1×10-3 mbar. The MIS thin film capacitor with the configuration of Si/Ta_2O_5/Al was fabricated by the deposition of aluminum as top electrode on Ta_2O_5 by vacuum evaporation.

The Ta_2O_5 films formed on silicon substrates were characterized by studying the chemical binding configuration, electron core level binding energies, crystallographic structure, current – voltage (I-V) and capacitance - voltage (C-V) measurements. The X-ray photoelectron spectroscopic (XPS) measurements were carried out by employing Physical Electronics (model PHI 5700) spectrometer to determine the core level binding energies of the deposited films. The crystallographic structure of the films was recorded in the 2θ range 30 - 65° using X-ray diffractometer (Seifert model 3003 TT). The lattice parameter of the films was calculated from the interplanar spacing (d) using the relation

$$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \qquad (1)$$

where h, k and l are the Miller indices. The capacitance - voltage characteristics of the fabricated Si / Ta_2O_5 / Al capacitors were measured by using Mioki (model 3532-

50) LCR meter. The current - voltage characteristics of the capacitor was measured using Hewlett Peckard (model HP 4140 B) PA meter. The dielectric constant (ε_r) of the films was calculated from the C-V measurements using the formula

$$\varepsilon_r = C.d/\varepsilon_o . A \qquad (2)$$

where C is the capacitance, d the thickness of the dielectric, A the area of the electrode and ε_o the permittivity of the free space. The optical transmittance (T) and reflectance (R) of the films were recorded using Hitachi (model U-3400) UV-Vis-NIR double beam spectrophotometer in the wavelength range 200 – 800 nm. The optical absorption coefficient (α) was calculated using the equation

$$\alpha = (1/d)\ [\ln T/(1-R)^2] \qquad (3)$$

The dependence of absorption coefficient on the photon energy ($h\upsilon$) was fitted to the relation for direct transition between the top of the valance band and the bottom of the conduction band using the relation

$$\alpha h\upsilon = A\ (h\upsilon - E_g)^{1/2} \qquad (4)$$

where E_g is the optical band gap of the film and A the absorption edge width parameter. The optical band gap of the films was evaluated from the extrapolation of the linear portion of the plots of $(\alpha h\upsilon)^2$ versus photon energy to $\alpha = 0$.

3. Results and discussion

The Ta_2O_5 films deposited by rf magnetron sputtering were an analysed by X-ray photoelectron spectroscopy to determine the core level binding energies of the films. Fig. 1 shows the narrow scan x-ray photoelectron spectra in the binding energy range 24 - 30 eV for the core level binding energy of Ta 4f and 527 – 533 eV for O 1s of Ta_2O_5 films formed at different oxygen partial pressures. The films formed at low oxygen partial pressure of 5×10^{-5} mbar gives rise to two peaks at 25.3 and 27.2 eV for Ta $4f_{7/2}$ and Ta $4f_{5/2}$ core levels of Ta 5^+. The films deposited at oxygen partial pressure of 1×10^{-4} mbar exhibited the Ta $4f_{7/2}$ peak at 26.3 eV and Ta $4f_{5/2}$ peak at 28.2 eV. The core level binding energy of pure metal Ta $4f_{7/2}$ was 21.8 eV [14] and tantalum oxide Ta $4f_{7/2}$ was 26.5 eV [15]. This indicated that the tantalum atoms in the films were positively charged relative to that of Ta metal by formation of direct bonds with oxygen [7]. The core level binding energy of O 1s of the films formed at oxygen partial pressure of 5×10^{-5} mbar was 530.1 eV, while at oxygen partial pressure of 1×10^{-4} mbar, it shifted to 530.3 eV. It is to be noted that the stoichiometric Ta_2O_5 films ontained the Ta $4f_{7/2}$ peak at 26.3 eV [16]. High core level binding energy of 26.8 eV was also observed in ion-beam deposited [17] and laser induced chemical vapor deposited films [15]. These results indicated that films formed at the oxygen partial pressure $\geq 1\times10^{-4}$ mbar were stoichimetric.

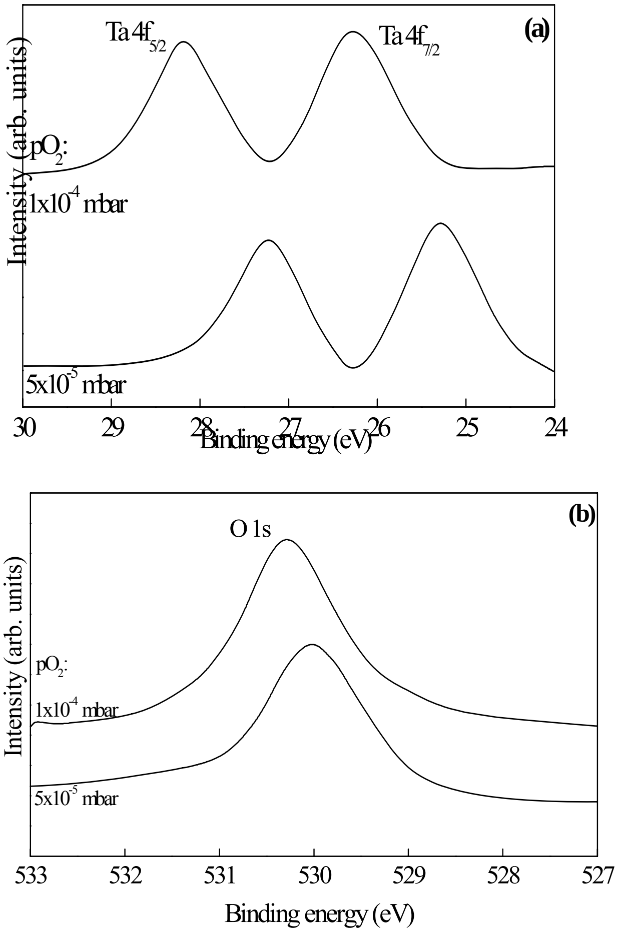

Fig. 1. XPS core level binding energy spectra of Ta_2O_5 films, (a) Ta 4f and (b) O 1s.

X-ray diffraction profiles of Ta_2O_5 films formed at different oxygen partial pressures are shown in Fig. 2. The presence of diffraction peaks indicated the polycrystalline nature of the films. The films formed at low oxygen partial pressure of 5×10^{-5} mbar showed reflections at $2\theta = 32.60$, 40.85, 39.51, 44.50 and 59.30°. The reflections observed at 39.51, 44.50 and 59.30° related to the (261), (330) and (400) planes of tantalum oxide. The peaks located at 32.60 and 40.85° corresponds to the unoxidized tantalum. It revealed that the films formed at low oxygen partial pressure showed the mixed phase of tantalum and tantalum oxide due to insufficient oxygen in the sputter chamber. As the oxygen partial pressure increased to 1×10^{-4} mbar only the reflections (261), (330) and (400) of Ta_2O_5 were observed. It indicated that the films formed at an oxygen partial pressure of 1×10^{-4} mbar were single phase Ta_2O_5. These single phase films showed the lattice parameters a = 6.226 Å, b = 40.950 Å and c = 3.684 Å with orthorhombic β-phase of Ta_2O_5, which was in good agreement with the JCPDS data [18]. The increase in the peak intensity with the increase of oxygen partial pressure attributed to the improvement in the crystallinity of the films. The crystallite size of the films calculated from the full width at half maximum of the X-ray diffraction peaks increases from 8 to 20 nm with the increase of oxygen partial pressure from 5×10^{-5} to 5×10^{-4} mbar.

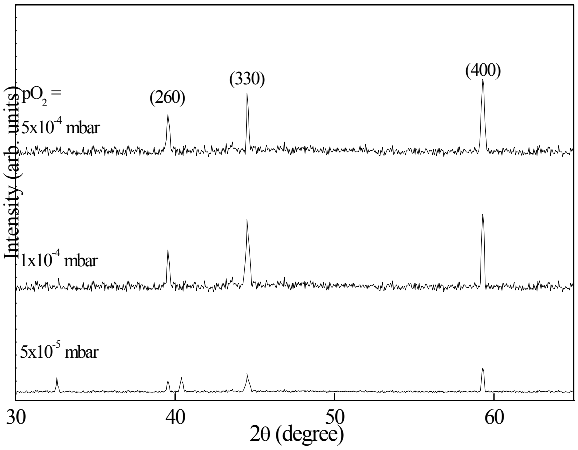

Fig. 2. X-ray diffraction patterns of tantalum oxide films.

The capacitance and dissipation factor (tan δ) of the films were determined at the frequency of 1 MHz from the capacitance-voltage measurements. The capacitance of the films increased from 9.3×10^{-12} to 1.4×10^{-11} F with the increase of oxygen partial pressure from 5×10^{-5} to 5×10^{-4} mbar. The dissipation factor of the films decreased from 0.12 to 0.04 with the increase of oxygen partial pressure. The increase of capacitance and decrease of dissipation factor with the increase of oxygen partial pressure from 5×10^{-5} to 5×10^{-4} mbar could be due to improvement in the crystallinity of the films.

The dielectric constant of the films was calculated at the frequency of 1 MHz. Fig. 3 shows the dependence of dielectric constant of Ta_2O_5 films formed at different oxygen partial pressures. The dielectric constant of the films increased with the increase of oxygen partial pressure. The low value of dielectric constant of 17 in the case of the films formed at low oxygen partial pressure of 5×10^{-5} mbar was due to the presence of mixed phase of tantalum and tantalum oxide. The increase of dielectric constant to 22 in the case of the films formed at 5×10^{-4} mbar was due to the improvement in the crystallinity and the packing density. Such an increase in the dielectric constant was also noticed by Atanassiva et al. [19] due to improvement in the crystallinity of the tantalum oxide films.

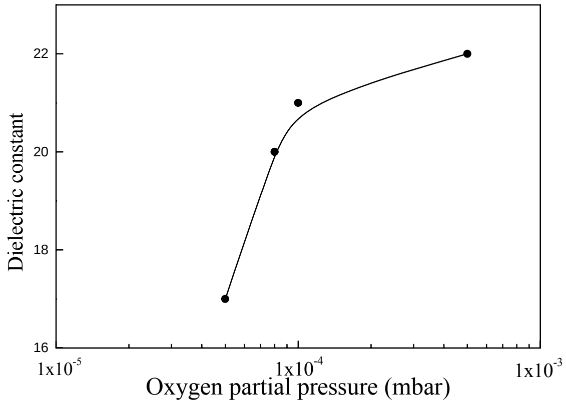

Fig. 3. Variation of dielectric constant of Ta_2O_5 films with the oxygen partial pressure.

Fig. 4 shows the current - voltage characteristics of Ta_2O_5 films at different oxygen partial pressures. At low oxygen partial pressure of 5×10^{-5} mbar the leakage current density (-1 V) was 1×10^{-7} A/cm². The leakage current density decreased to 4×10^{-9} A/cm² with the increase of oxygen partial pressure to 1×10^{-4} mbar may be due to the reduction in the oxygen vacancies and bond defects in the initial oxide as well as enhancement of the interfacial properties [20].

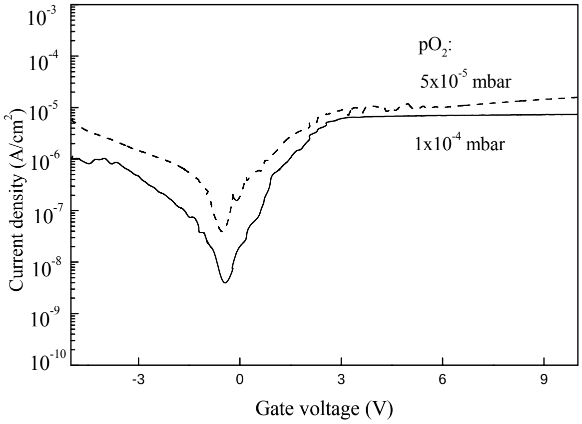

Fig. 4. Current – voltage characteristics of Ta_2O_5 capacitors formed at different oxygen partial pressures.

The optical transmittance spectra of tantalum oxide films formed at different oxygen partial pressures are shown in Fig. 5. The films formed at low oxygen partial pressure of 5×10^{-5} mbar showed low optical transmittance. This low optical transmittance was due to the presence of the metallic tantalum along with the tantalum oxide. The metallic tantalum atoms act as scattering centers for light hence the optical transmittance was decreased. When the oxygen partial pressure reached to 1×10^{-4} mbar the optical transmittance increased because of the single phase of tantalum oxide. The optical absorption edge of the films shifted towards higher energy side with the increase of oxygen partial pressure. The optical band gap of the films increased from 4.36 to 4.44 eV with the increase of oxygen partial pressure from 5×10^{-5} to 5×10^{-4} mbar. The optical band gap of the single phase Ta_2O_5 films formed at oxygen partial pressure of 1×10^{-4} mbar was 4.40 eV, which is in good agreement with the dc magnetron sputtered films [21].

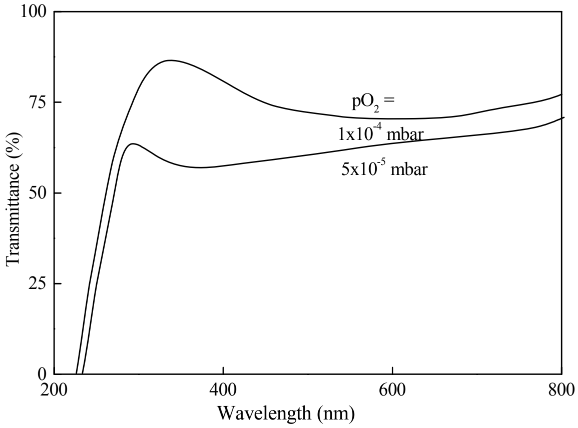

Fig. 5. Optical transmittance spectra of tantalum oxide films.

4. Conclusions

Thin films of Ta_2O_5 were formed on silicon and quartz substrates by rf magnetron sputtering of tantalum target under various oxygen partial pressures in the range 5×10^{-5} - 5×10^{-4} mbar. The influence of oxygen partial pressure on the chemical binding configuration, structure, electrical and optical properties was studied. The X-ray photoelectron spectroscopic studies revealed that the films formed at oxygen partial pressure $\geq 1\times10^{-4}$ mbar were stoichiometric. The crystallite size of the films increased from 15 to 25 with the increase of oxygen partial pressure from 5×10^{-5} to 5×10^{-4} mbar respectively. The dielectric constant increased from 17 to 22 with the increase of oxygen partial pressure, due to improvement in the crystallinity and packing density of the films. The low leakage current density of 4×10^{-9} A/cm^2 was observed in the single phase Ta_2O_5 films. The optical band gap of the films increased from 4.36 to 4.44 eV with the increase of oxygen partial pressure. In conclusion, single phase orthorhombic β-phase Ta_2O_5 films with dielectric constant of 21, low leakage current density of 4×10^{-9} A/cm^2 and optical band gap of 4.40 eV were obtained at an oxygen partial pressure of 1×10^{-4} mbar.

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