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Interface of tantalum oxide films on silicon by UV annealing at low temperature

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Abstract

In previous work, we have grown 4–10 nm Ta_2O_5 films by photo-induced chemical vapour deposition (photo-CVD) using a special precursor injection system, which exhibited leakage currents as low as 2.19×10^{-7} A/cm^2 at 1 MV/cm. However properties of these films are known to deteriorate with decreasing film thickness. UV annealing at low temperatures using an excimer UV source can improve the electrical properties of these films dramatically. In this paper, tantalum pentoxide thin films with thicknesses of approximately 40 nm grown by photo-CVD have been annealed at low temperature using an excimer UV lamp. Film properties have been characterised using ellipsometry, Fourier transform infrared spectroscopy, UV spectrophotometry, capacitance–voltage and current–voltage techniques. After UV annealing, improved leakage current densities as low as 4.0×10^{-8} A/cm^2 at 1 MV/cm, and breakdown fields higher than 3.0 MV/cm can be achieved. Investigation of the interfacial SiO_x layer formed during deposition and after UV annealing by X-ray photoelectron spectroscopy and TEM reveals that thickness increases with UV annealing time and that the suboxides in the film and at the interface are converted into stoichiometric oxide, leading to an improvement of the electrical properties.

Keywords: UV annealing; Tantalum pentoxide; Gate dielectrics; Interfacial SiO_x layer

1. Introduction

We have previously reported the growth of 4–10 nm Ta_2O_5 films on c-Si by photo-induced chemical vapour deposition (photo-CVD) using 222 nm excimer lamps and a special precursor injection system, which exhibited leakage currents as low as 2.19×10^{-7} A/cm^2 at 1 MV/cm [1–3]. These layers were nonstoichiometric and their optical and electrical properties were strongly affected by both the O/Ta ratio and their interfacial properties. More recently we have found that UV annealing at low temperatures can significantly improve the electrical properties of these films [4–8]. In this paper, we investigate the interface changes in the $Ta_2O_5/SiO_2/Si$ system as a function of UV annealing using X-ray photoelectron spectroscopy (XPS), FTIR and TEM. Improvements in both the interfacial and electrical properties of these layers by UV annealing in pure oxygen and other atmospheres are also discussed.

2. Experimental details

The experiments were performed on n-type 4-in. Si (1 0 0) substrates (resistivity 2–4 Ω cm (i.e. $N_d\sim1\times10^{15}$/cm^3), which received a standard FSIB clean. Tantalum tetraethoxy dimethylaminoethoxide ($Ta(OEt)_4(dmae)$) (made by Inorgtech. Ltd, UK), dissolved in an anhydrite cyclohexane solvent (10%), was the precursor used. Nitrous oxide (N_2O) was introduced as the oxidising agent at a fixed flow rate of 20 sccm. A 60 sccm argon plus 20 sccm N_2O gas flow carried

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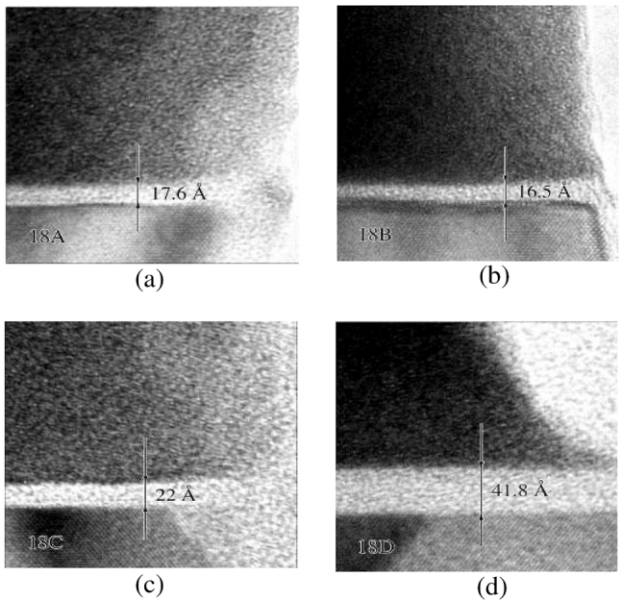

Fig. 1. TEMs of cross-section of as-deposited and UV annealed Ta_2O_5 films, (a) as-deposited; (b) 10 min UV annealed; (c) 15 min UV annealed; (d) 40 min UV annealed.

the precursor through a showerhead at 110 °C to the Si (1 0 0) wafers, which were maintained at a temperature of 350 °C during the deposition. UV annealing was performed in 1000 mbar of high purity oxygen (99.999%). The photo-CVD reactor used comprised of two stainless steel chambers separated by a quartz window transparent to the UV light. The UV radiation, centered at 222 nm in a narrow emission band, was generated by a dielectric barrier discharge from a gas mixture of krypton and chlorine in the top chamber on to the sample surface. The more details of this source and the complete photo-CVD apparatus used have been described in previous papers [1,5,9–11]. An FTIR spectrometer (Paragon 1000, Perkin–Elmer) and ellipsometer (Rudolph AutoEL II) were employed to examine the composition, chemical structure, film thickness and refractive index of the films. Surface and interface properties were analysed by XPS in an ESCALAB MK II system with a Mg Kα ($h\nu = 1253.6$ eV) radiation source. Photoelectrons were collected at an emission angle of 15° with respect to the surface normal. The depth profiles of Ta, O, Si and C in the samples were determined by Ar^+-ions (3 keV) with a current of 20 μA. The ratio of the oxygen to tantalum content in the films was determined by peak deconvolution of the XPS curves. MOS capacitors were fabricated using the Ta_2O_5 layers grown and annealed by this UV-CVD process by incorporating an evaporated Al top contact of area 8×10^{-4} cm^2. The electrical properties of the films were measured using HP4140 and HP4275 systems at a frequency of 1 MHz.

Table 1
Thickness of the SiO_2 interface between UV-CVD Ta_2O_5 films and Si measured by TEM and ellipsometry for 10, 15 and 40-min annealing times, respectively

UV annealing time (min)	Refractive index of Ta_2O_5 films	Thickness of Ta_2O_5 films by ellisometry (nm)	Thickness of Ta_2O_5 films by TEM (nm)	Thickness of SiO_2 films by TEM (nm)
0	2.005	50.0	44	1.76
10	2.012	41.4	37.8	1.65
15	2.041	43.7	38.2	2.20
40	2.150	46.4	40.2	4.18

3. Results and discussion

Films with thickness approximately 40 nm deposited at a temperature of 350 °C, were UV annealed in 1000 mbar in pure oxygen at 350 °C for 10, 15 and 40 min, respectively. Fig. 1 shows TEM cross-section images of these layers. As can be seen the Ta_2O_5 films (top layer) are amorphous in both the as-deposited and UV annealed states. This was also confirmed by XRD [7]. Also the interfacial layer remains constant during 10-min annealing and then increases with annealing time up to 40 min. This interface was confirmed to be SiO_2 by XPS, and will be discussed later. Table 1 presents details of the interfacial properties measured by both TEM and ellipsometry.

Fig. 2 presents the O_{1s} peaks for films as-deposited and annealed for 15 and 40 min. For the as-deposited film, the main peak centered at a binding energy approximately 531.15 eV corresponding to the Ta–O bond in Ta_2O_5 [7]. The main peak of the Ta–O bond annealed for 15 min does not appreciably change. A slight increase in the peak intensity may suggest that more Ta–O bonds were formed during the UV annealing step. However, after UV annealing for 40 min this main peak has shifted to 531.65 eV. It is well known that a peak at 532.55 eV corresponds to Si–O bonds [7,12]. Thus this XPS peak shift to a higher binding energy

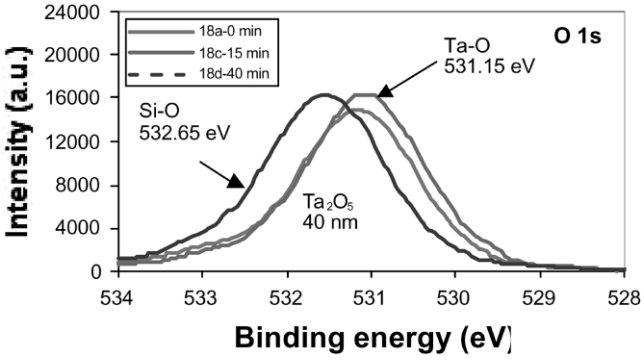

Fig. 2. XPS of O_{1s} peaks for as-deposited and 15 and 40 min annealed films.

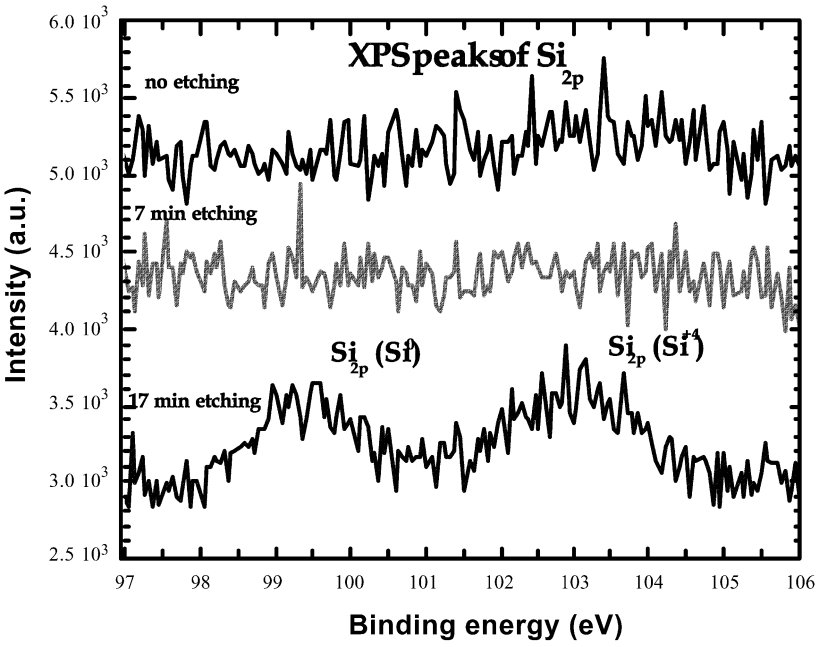

Fig. 3. XPS profile of Si_{2p} peak of 15 min annealed films.

may suggest that more Si–O bonds were formed during UV annealing.

Fig. 3 shows the Si_{2p} peaks of the films annealed for 15 min and then Ar^+-etched for 7 and 17 min. No peaks were detected from the surface of the annealed films, without etching, or etched for 7 min. However, two peaks were observed from the annealed film etched for 17 min. The peak centered at a binding energy approximately 99.45 eV corresponds to Si–Si bonds from the Si substrate and the other peak centered at approximately 103.15 eV corresponds to Si–O bonds from the interfacial layer. This indicates that UV annealing promotes interface SiO_2 layers. Fig. 4 compares the Ta_{4f} peaks of the as-deposited and 15 min annealed samples. It is noted that the Ta_{4f} spectrum for the as-deposited sample has a tail toward the lower binding energy side of the main peak. It is believed that such a tail reflects the low valency of the tantalum in the as-deposited film. However, this tail disappears from the spectrum of the annealed film. This is further evidence that UV annealing can convert the suboxides from the as-deposited layer into stoichiometric Ta_2O_5.

Fig. 5 gives the atomic ratio of O/Ta in the Ta_2O_5 films with UV anneal time on the surface and after 7 min etching. The atomic ratio of O/Ta in the surface of the Ta_2O_5 film is higher than that for stoichiometric Ta_2O_5 due to physisorbed oxygen [13]. The atomic ratio of O/Ta inside the Ta_2O_5 film is approximately 2.0 for

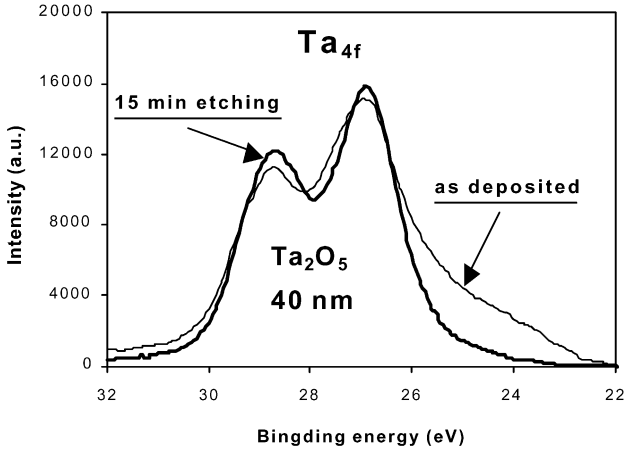

Fig. 4. XPS of Ta_{4f} peaks for the as-deposited and 15 min annealed films.

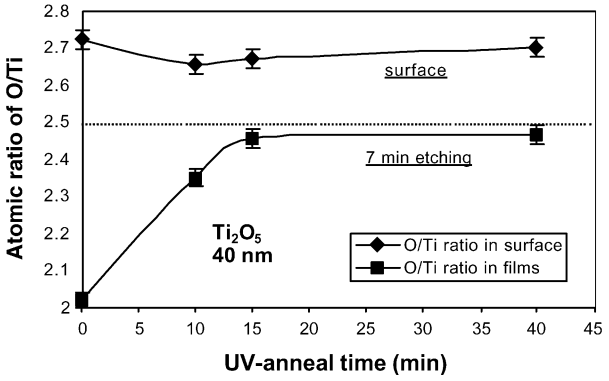

Fig. 5. Atomic ratio of O/Ta of the Ta_2O_5 films with anneal time at the surface (top) and after 7 min etching (bottom).

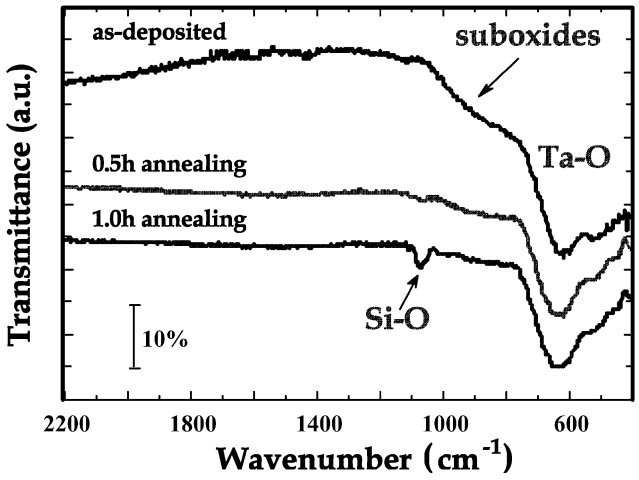

Fig. 6. FTIR spectra of Ta_2O_5 films deposited at a temperature of 350 °C and annealed for 30 and 60 min.

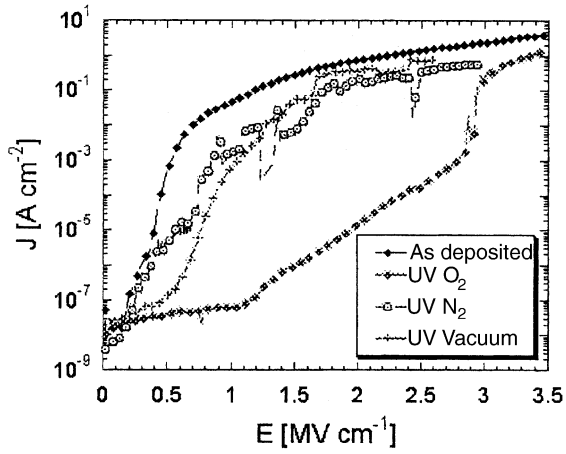

Fig. 7. JE profiles for as-deposited, 15 min O_2, vacuum and N_2 annealed samples.

the as-deposited samples. However, this increases to 2.46 with UV annealing time, close to stoichiometric value of 2.50. This result clearly indicates that suboxides exist in the as-deposited Ta_2O_5 film. The oxygen species produced during the UV annealing process are readily adsorbed onto the surface and then diffuse into the film to react with oxygen vacancies. It noted that the atomic ratio of O/Ta remains constant even with increased annealing time. As diffusing oxygen species arrive at the underlying interfaces of the $Ta_2O_5/SiO_2/Si$ system, interfacial reactions between the silicon and the oxygen species occur and the SiO_2 layer increases in thickness as Fig. 1 has shown.

To confirm the effect of UV annealing on converting suboxides and forming SiO_2 at the interface, a further experiment using longer UV annealing times has been carried out. Fig. 6 shows the FTIR spectra in the 400–2200/cm range of the Ta_2O_5 films deposited at a temperature of 350 °C and UV annealed for 30 and 60 min. As can be seen, a dominant absorption band approximately 650/cm, associated with Ta–O–Ta and Ta–O stretching vibration modes, is observed. However, a broad absorption band between 800 and 1000/cm, corresponding to the presence of Ta suboxides, is greatly reduced after 30-min annealing. This broad peak is further slightly reduced for 60-min annealing. However, a new peak appears at 1075/cm, which is due to the SiO_2 stretching vibration. That indicates that not only are the suboxides in the film converted into more stoichiometric Ta_2O_5 but that SiO_2 can be formed at the interface of the film during annealing. Fig. 7 shows the *I–V* profiles for as-deposited films, together with those for layers annealed for 15 min in O_2, as well in vacuum and in N_2. After UV oxygen annealing, the leakage current densities have improved to as low as 4×10^{-8} A/cm^2 at 1 MV/cm. For these layers breakdown fields higher than 3.0 MV/cm can be achieved. It is also evident from the figure that the improvement in the electrical properties for the vacuum and N_2 annealed cases is only marginal. These results provide strong evidence that optically excited oxygen species must be present to induce the required annealing process.

4. Conclusions

UV annealing of photo deposited Ta_2O_5 films has been performed in 1000 mbar of pure oxygen under various conditions, leading to an increase in thickness of the interfacial layer with Si and a dramatic improvement of the layer electrical properties. This improvement is due to conversion of suboxides in the layer into more stoichiometric Ta_2O_5 and the formation of SiO_2 at the interface of the Ta_2O_5 with Si. Reactive oxygen radicals formed by the high photon energy of the 222 nm excimer lamps provide a source to promote rapid oxidation in the as-deposited films. Post-deposition UV annealing experiments in oxygen-deficient (vacuum and N_2) conditions are found not to improve the properties of the as-deposited layers. The technique is currently being extended to other high-*k* dielectrics, using related carbon based metal–organic precursors.

Acknowledgments

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