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High Energy Photoemission study of Ta_2O_5 grown on Si

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Abstract : Good quality Ta_2O_5 films of thickness less than 1 nm were deposited on p-type Si(100) and investigated the thermal stability in Ultra High Vacuum (UHV). As deposited films contained very little sub-oxide of Si which transformed into SiO_2 upon vacuum or oxygen annealing. Decomposition of Ta_2O_5 on Si(100) started at around 550^0C and completely got converted to sub Ta oxides at 750^0C. Flashing at about 850^0C produced a doublet structure indicative of stable sub Ta oxides. Similar doublet structure was observed for Ta sub oxide films independently prepared but were not observed for Ta silicide films. As deposited Ta_2O_5 films consumed considerable amount of oxygen when annealed under ambient oxygen indicating oxygen deficiency in as-deposited films.

Keywords : Photoelectron Soectroscopy, Synchrotron radiation, Oxide, Thin film, Annealing

PACS Numbers : 79.60.-I, 79.60.Dp, 68.47.Gh

I. Introduction

Tantalum pentoxide (Ta_2O_5) occupies an important place in semiconductor industry due to its high dielectric constant of about 25 [1]. Interestingly, dielectric constant of Ta_2O_5 can be enhanced to 110 by nitridation [2]. Ta_2O_5 can also be used as an insulating layer in thin film electroluminescent devices, optical wave guides, sensor layer in chemical and biological environment [3]. Ta_2O_5 is a challenging material in the fundamental point of view. Crystal structure of Ta_2O_5 poses challenges to crystallographers for more than 50 years [4]. Crystallinity of Ta_2O_5 films show an improvement by the addition of water vapor into the working gas [5].

Tantalum possesses several valence states and easily forms compounds with reactive elements such as oxygen or silicon. It forms variety of oxides [6] when exposed to oxygen and can form various silisides with silicon [7]. On high temperature annealing Ta/Si(100) exhibits interesting microstructure of concentric ring patterns with composition $TaSi_2$[7]. XPS studies of Ta_2O_5 deposited on Si substrate showed a depth dependent concentration profiles with Ta_2O_5 on the surface and the sub Ta oxides with increasing depth [8]. In general, composition of the sub-oxide phases of tantalum and their chemical shifts appear to be controversial [9]. Chemistry of Ta-O system is complicated due to the multiple oxidation states of Ta and this complication becomes many fold in Ta-Si-O system due to the possible Ta-Si, Si-O, Ta-O and Ta-Si-O reactions.

In this paper, we report the high energy and high resolution XPS studies of UHV annealed in-situ prepared Ta_2O_5 in oxygen pressure.

II. Sample Preparation

Pure Tantalum was deposited on p-type Si(100) substrate using e-beam evaporation technique in-situ in the preparation chamber of THE-XPS machine at BW2 beamline of HASYLAB. Base pressure of the chamber was maintained below $2.0x10^{-9}$ mbar. Prior to the deposition, Si substrate was flashed few times at 960^0C until a good p(2x1) LEED pattern was observed. Surface cleanliness of the substrate was checked by XPS at grazing X-ray incidence and found no traces of carbon or oxygen on the surface in all cases. Chamber was back filled with oxygen to the required pressure for preparing the Ta penta-oxide samples.

III. Results and Discussion

Samples were investigated by high energy XPS technique with a photon energy of 3000 eV. Total resolution of the spectrometer was 0.45 eV measured as the FWHM of the Ag $3d_{5/2}$ of clean Ag foil. Ta $4f_{7/2}$ of the Ta foil with native oxide was used for B.E. referencing which occurs at 21.5 eV when calibrated using Au $4f_{7/2}$ at 83.96 eV. Measurements were performed at X-ray grazing incidence to enhance the surface sensitivity.

Figure 1 shows Ta 4f and O 1s spectra of Ta_2O_5 grown on Si(100). Annealing the film in an oxygen ambient of $1.5x10^{-4}$ mbar at 650^0C exhibited a small feature with a c.s. of 1.1 eV. After annealing, pentoxide peaks shifted to high B.E. by about 0.4 eV. Si 1s spectra (not shown) of as deposited film showed some sub-oxides of Si. After oxygen annealing Si 1s peak shifted to high B.E. by 0.2 eV due to the interfacial SiO_2 which is observed at 4.7 eV higher B.E. from the main Si peak. O 1s peak (Figure 1, lower panel) showed a large shift of 1.0 eV towards high B.E. after annealing.

Interestingly, width of O 1s peak remained the same but the little asymmetry on high B.E. side of the as deposited sample disappeared after annealing. Intensity of O 1s peak increased by a factor of 2 after annealing. The low B.E. feature developed after annealing in Ta 4f spectra has the B.E. (1.1 eV) close to the value observed for Ta_2O (1.0 eV).

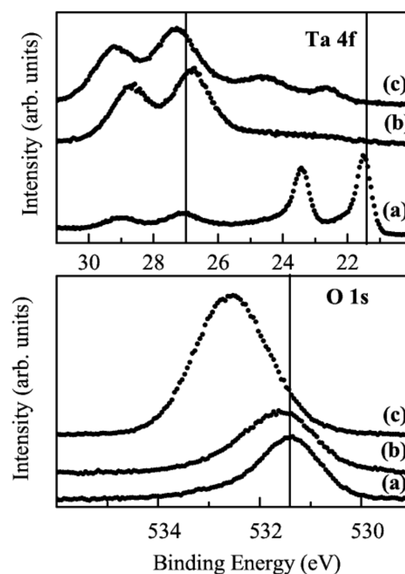

Fig. 1: XPS spectra of O 1s and Ta 4f (a) Ta foil (b) as deposited Ta_2O_5 on Si(100) (c) annealed Ta_2O_5 at 650^0C

Ta_2O_5 deposited at temperatures below 600^0C is known to form amorphous phase on Si(100). Between 600^0C and 700^0C these films start to crystallize in hexagonal delta-Ta_2O_5 and this phase transforms into L-(orthorhombic) phase above 800^0C. As deposited pure Ta_2O_5 a chemical shift of 5.3 eV that is slightly smaller than the one observed on Ta foil (5.6 eV) with native oxide indicating oxygen defects in as deposited film. Annealing Ta_2O_5 at 650^0C in oxygen ambient enhanced the intensity of the O 1s peak by about 100% (Figure 1). As grown Ta_2O_5 in amorphous form contains lot of oxygen defects as indicated by the lower chemical shift of Ta 4f. This extra amount of oxygen is consumed in stabilizing the poly-crystalline phase of Ta_2O_5 from amorphous Ta_2O_5. This phase becomes δ-(hexagonal) Ta_2O_5 after annealing. The B.E. shifts of Ta 4f (0.4 eV) and O 1s (1.0 eV) after oxygen annealing can be attributed to this structural transition. Anomalously large O 1s chemical shift clearly indicates the structural transformation after annealing in oxygen ambient. Little amount of lower Ta oxide formed after annealing could be due to insufficient oxygen pressure to completely stabilize crystalline Ta_2O_5.

IV. Conclusion

In summary, we have grown Ta pentoxide by depositing Ta onto Si(100) in UHV and in oxygen ambient. Highly stable TaO and Ta_2O_{1+x} formation occurred only after high temperature annealing. Only, these two oxide phases survived after flashing the samples at 1000^0C. As deposited Ta_2O_5 formed in amorphous phase with oxygen deficiency and the transformation to poly-crystalline phase occurred upon annealing at 650^0C under oxygen ambient. This phase transition consumed lot of extra oxygen from the oxidizing agent.

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