1799
doi:10.1017/S1431927615009770 Paper No. 0898
Microsc. Microanal. 21 (Suppl 3), 2015

Aluminum and Tantalum Doping of Sputtered TiO_2 Thin Films

Inga Goetz[1], Rong Liu[2], Richard Wuhrer[3] and Leigh Sheppard[4]

[1] Flensburg University of Applied Sciences, Germany
[2] Advanced Materials Characterisation Facility, University of Western Sydney, Australia
[3] SIMS Facility, University of Western Sydney, Australia
[4] School of Computing, Engineering, and Mathematics, University of Western Sydney, Australia

TiO_2 is a promising material for the generation of hydrogen fuel from the photoelectrochemical splitting of water using sunlight [1]. In this application, performance is determined by the ability to generate electron-hole pairs during illumination, and keep them separated long enough to do useful work. A TiO_2-based homojunction, consisting of a graded composition is considered promising for this role [2]. The use of magnetron sputtering is considered promising for the fabrication of such a material.
The aim of this project is to explore the deposition of Al and Ta doped TiO_2 films and identify deposition parameters that facilitate control of film crystallinity, control of doping level and control film thickness. Meeting these aims will provide the basis for fabricating TiO_2-based homojunctions.

All films were prepared using the UWS Reactive Magnetron Sputtering Facility. A number of deposition parameters were tested including Ar:O_2 ratio, deposition pressure, source power and types (DC or RF), RF substrate bias voltage, and substrate temperature. The films were deposited onto substrates of titanium foil, silicon wafer (001), and glass, after initial evacuation to $< 5 \times 10^{-6}$ Torr. The films were then characterised using a Jeol 7001F Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) and a Bruker D8 Advance X-ray Diffraction (XRD). A Secondary Ion Mass Spectrometer (Cameca IMS 5FE7 – SIMS) was applied to determine the doping gradient of two graded films.

Tantalum, in contrast to both titanium and aluminium, showed very high deposition rates. The power levels for the initial films were set at 200W DC, 100W RF, and 50W DC for Ti, Al, and Ta respectively. 10 and 1.5 mTorr were chosen as deposition pressures to reflect the poisoning regime.

The initial Al-doped films exhibited a bimodal particle size distribution and increased surface roughness when deposited at 10 mTorr in comparison to the 1.5 mTorr films. Al-doping levels obtained from EDS were around 20% lower at 1.5 mTorr. The initial Ta-doped films showed even higher dopant concentrations and consisted predominantly of Tantalum. All of the initial films were found to be amorphous.

To control and reduce doping levels, power levels and types were adjusted for all elements. Ta doping levels were significantly reduced, even though a range of lower amounts would be desirable. Al concentrations also decreased, still a significant uncertainty persists concerning the actual values, as even an undoped sample showed significant amounts of Al in the EDS.

In comparison with the non-heated substrates, the heated samples with reduced dopant concentration exhibit a rougher surface structure and lower doping levels in the EDS analysis. Both the films grown on heated and non-heated substrates were found to consist of mixed amorphous, anatase and rutile phases. By varying the dopant power during deposition, two graded films were obtained, which exhibited the desired gradient in Ta concentration as determined by SIMS. These films demonstrate good control over thickness and composition, but further structural control is needed.

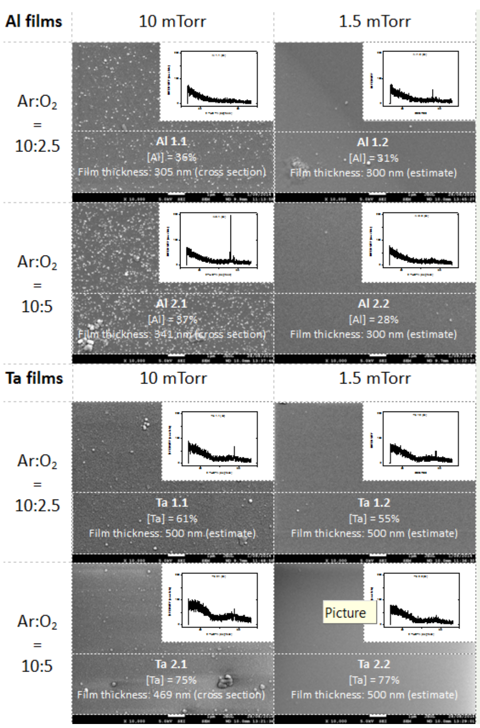

Figure 1: The initial set of 8 films (P(Ti) = 200W DC, no Bias, no heating) [Al] = (Al*100%)/(Al+Ti), [Ta] = (Ta*100%)/(Ta+Ti) (Al, Ta, Ti in at.%).

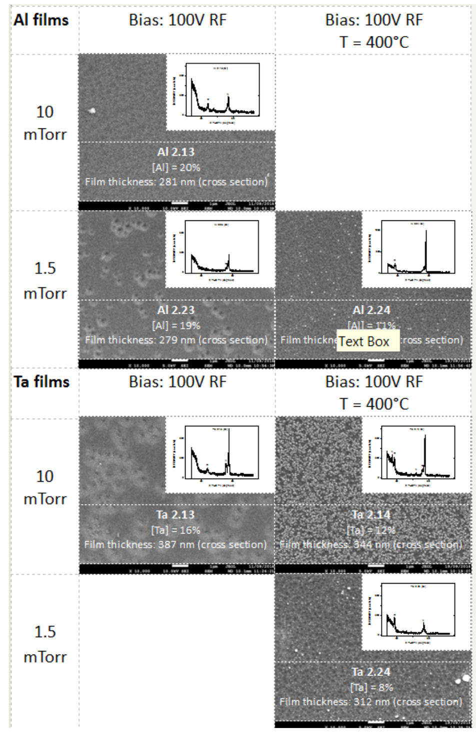

Figure 2: Films with lower dopant powers (P(Ti) = 2*200W DC, P(Ta) = 35W RF, P(Al) = 25W RF (30W RF for Al 2.24), Ar:O_2 = 10:5).

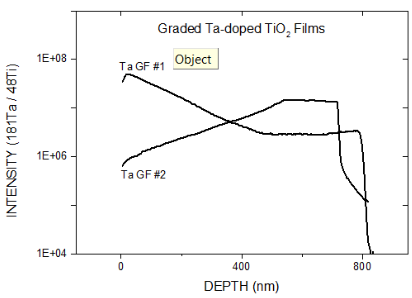

Figure 3: SIMS Results. Ta-doped graded films (P(Ta) = 35-100W RF, P(Ti) = 2*200W DC, 1.5 mTorr, Ar:O2 = 10:5, Bias: 100V RF, T = 400°C).

Al and Ta doped TiO_2 films have been successfully deposited using magnetron sputtering but with limited control. In particular, Ta doping at low levels (< 1 at.%) appears challenging. Al doping at low levels appears easier. Crystallinity is favoured by the application of substrate bias and heating but can yield a mix of anatase, rutile and amorphous phases. Control of film thickness was reliably obtained. Further investigations of the effect of Ar:O_2 and deposition pressure are required to tune the sputter yield of dopant sources.

References:

[1] Sheppard, L. R.; Nowotny, J. Materials for Photoelectrochemical Energy Conversion. Adv. Appl. Ceram. 2007, 106, 9-20

[2] Sheppard, L. R.; Dittrich, T.; Nowotny, M. K.; The Impact of Niobium Surface Segregation on Charge Separation in Niobium-Doped Titanium Dioxide, J. Phys. Chem. C, 2012, 116, 20923-20929

https://doi.org/10.1017/S1431927615009770 Published online by Cambridge University Press