Electronic Supplementary Information:

*In-situ* X-ray diffraction study of the controlled oxidation and reduction in the V-O system for the synthesis of VO$_2$ and V$_2$O$_3$

thin films

Geert Rampelberg,$^a$,* Bob De Schutter,$^a$ Wouter Devulder,$^a$ Koen Martens,$^b$ Iuliana Radu,$^b$ and Christophe Detavernier$^a$

$^a$ Department of Solid State Sciences, Ghent University, Krijgslaan 281/S1, 9000 Ghent, Belgium

$^b$ IMEC, Kapeldreef 75, 3001 Leuven, Belgium

* Corresponding author, e-mail: Geert.Rampelberg@UGent.be, tel: +32 9 264 4355
Oxidation in 0.2 mbar O$_2$

Figure 1 shows the in-situ XRD measurements of the oxidation of V films with thicknesses 20 nm, 40 nm and 80 nm on Al$_2$O$_3$ and SiO$_2$ in 0.2 mbar O$_2$ at 480°C. In all cases VO$_2$(R) is formed, characterized by a diffraction peak near 40 °, which corresponds with the (020) plane. Temperature dependent sheet resistance measurements for these oxidized films are shown in figure 2. The change in sheet resistance during transition varies between 2 and 3 orders of magnitude. All films show more or less the same absolute values, except from the thinnest film on SiO$_2$ which has an overall higher sheet resistance of approximately 2 orders of magnitude. Figure 3 shows SEM images of these VO$_2$ films. The morphology is clearly much different on the Al$_2$O$_3$ and SiO$_2$ templates. The grain sizes are much larger on SiO$_2$ and the thinnest film has even agglomerated, which explains the drastically increased sheet resistance. In the other cases, grain sizes are smaller when film thickness decreases.

Oxidation in a mixture of 50 mbar H$_2$ and 2 mbar O$_2$

Figure 4 shows the temperature dependent sheet resistance of the V films oxidized at 480°C in a mixture of 50 mbar H$_2$ and 2 mbar O$_2$. The change in sheet resistance during transition varies from approximately 2 orders of magnitude for the thinnest film to more than 4 orders of magnitude for the thickest film. Figure 5 shows the SEM images for these films. All films show a fine grained structure, with smaller grains compared to the films oxidized in 0.2 mbar O$_2$. The same trends are visible, i.e. grain size increases with film thickness and grains are larger on the SiO$_2$ template.

V$_2$O$_5$, V$_6$O$_{13}$ and V$_2$O$_3$

Apart from VO$_2$, three other vanadium oxide phases were prepared during this work. V$_2$O$_5$ was prepared by oxidation of 80 nm V in air at 480°C for 30 minutes. V$_6$O$_{13}$ was prepared by oxidation of 80 nm V in 2 mbar O$_2$ at 480°C for 60 minutes. V$_2$O$_3$ was prepared from the V$_2$O$_5$ film, by a subsequent reduction in 50 mbar H$_2$ at 480°C for 60 minutes. Figure 6 shows SEM images for these phases. All of these phases formed as continuous layers.
Fig. 1 *In-situ* XRD measurements during isothermal oxidation of 20 nm, 40 nm and 80 nm vanadium layers on the Al$_2$O$_3$ and SiO$_2$ templates at 480°C in an oxygen partial pressures of 0.2 mbar.
Fig. 2 Temperature dependent sheet resistance measurements after isothermal oxidation of 20 nm, 40 nm and 80 nm vanadium layers on the Al$_2$O$_3$ and SiO$_2$ templates at 480°C in an oxygen partial pressures of 0.2 mbar.
Fig. 3 SEM images of the films annealed at 480°C in 0.2 mbar O$_2$. 
Fig. 4 Temperature dependent sheet resistance measurements after isothermal oxidation of 20 nm, 40 nm and 80 nm vanadium layers on the $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ templates at 480°C in a mixture of 50 mbar $\text{H}_2$ and 2 mbar $\text{O}_2$. 
Fig. 5 SEM images of the films annealed at 480°C in a mixture of 50 mbar H₂ and 2 mbar O₂.
Fig. 6 SEM images of the $V_2O_5$, $V_6O_{13}$ and $V_2O_3$ thin films.