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_2O_3 thin films

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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_2O_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_2O_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_2O_5, V_6O_{13} and V_2O_3

Apart from VO_2, three other vanadium oxide phases were prepared during this work. V_2O_5 was prepared by oxidation of 80 nm V in air at 480°C for 30 minutes. V_6O_{13} was prepared by oxidation of 80 nm V in 2 mbar O_2 at 480°C for 60 minutes. V_2O_3 was prepared from the V_2O_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.

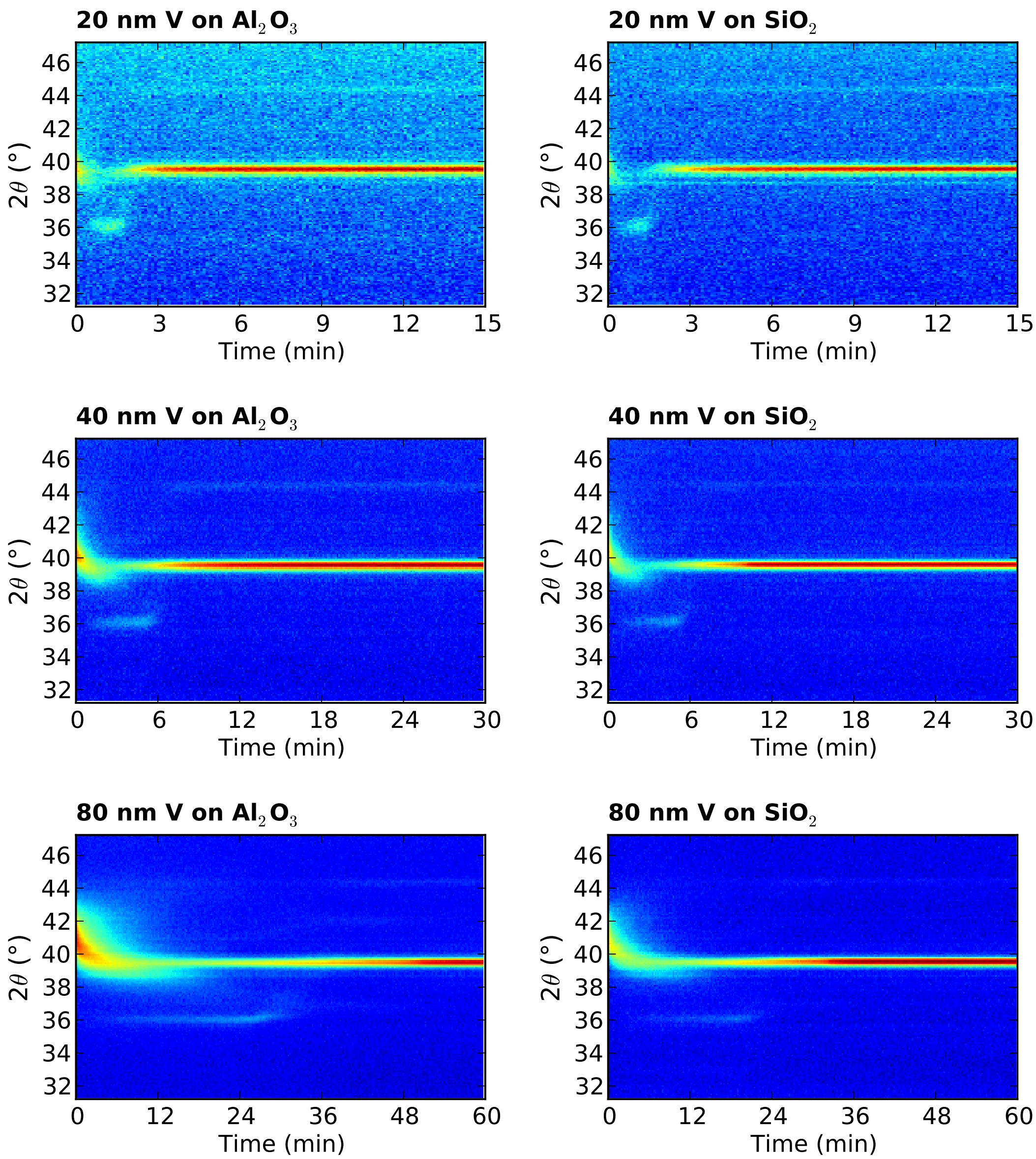

Fig. 1 *In-situ* XRD measurements during isothermal oxidation of 20 nm, 40 nm and 80 nm vanadium layers on the Al_2O_3 and SiO_2 templates at 480°C in an oxygen partial pressures of 0.2 mbar.

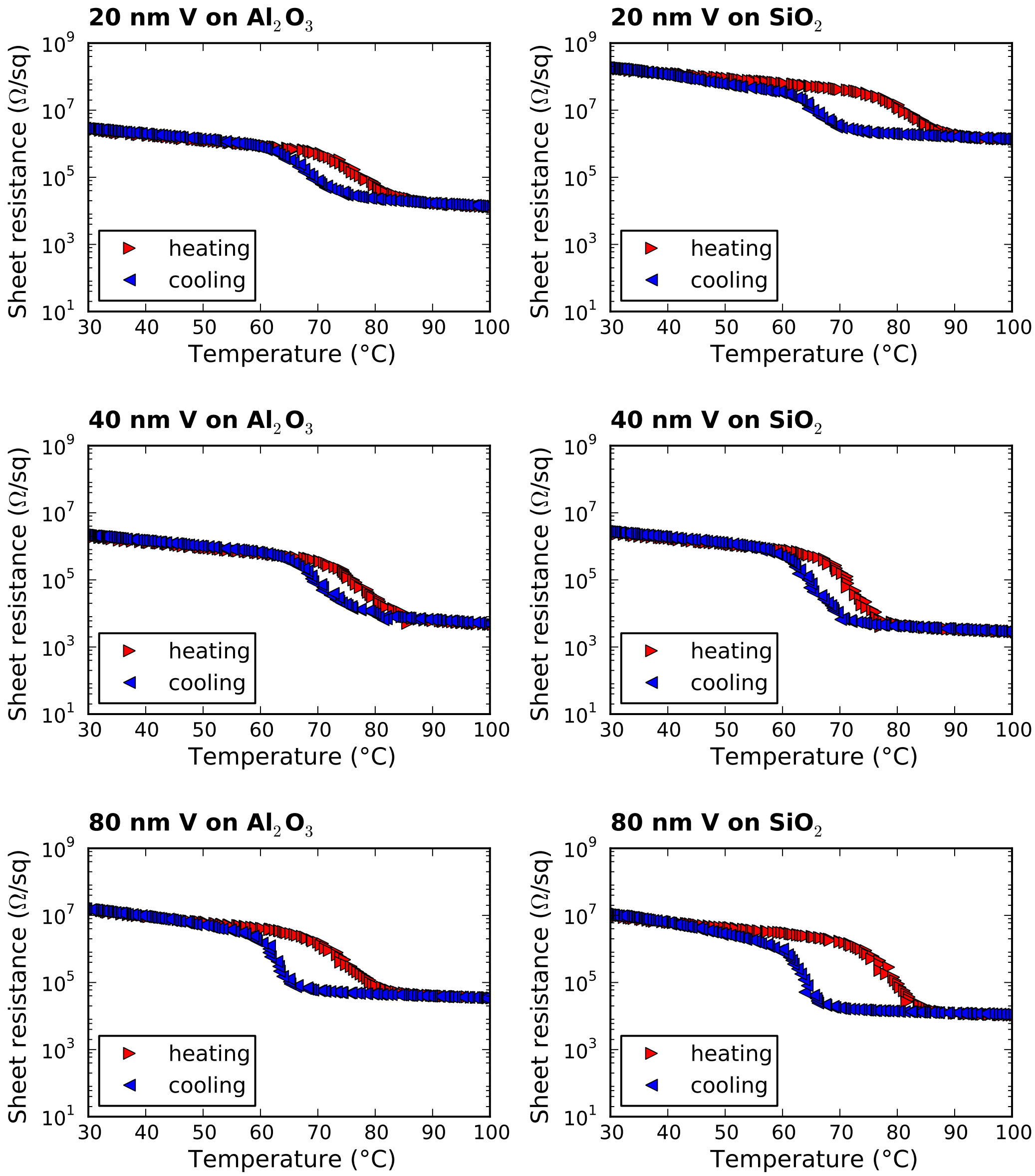

Fig. 2 Temperature dependent sheet resistance measurements after isothermal oxidation of 20 nm, 40 nm and 80 nm vanadium layers on the Al_2O_3 and SiO_2 templates at 480 °C in an oxygen partial pressures of 0.2 mbar.

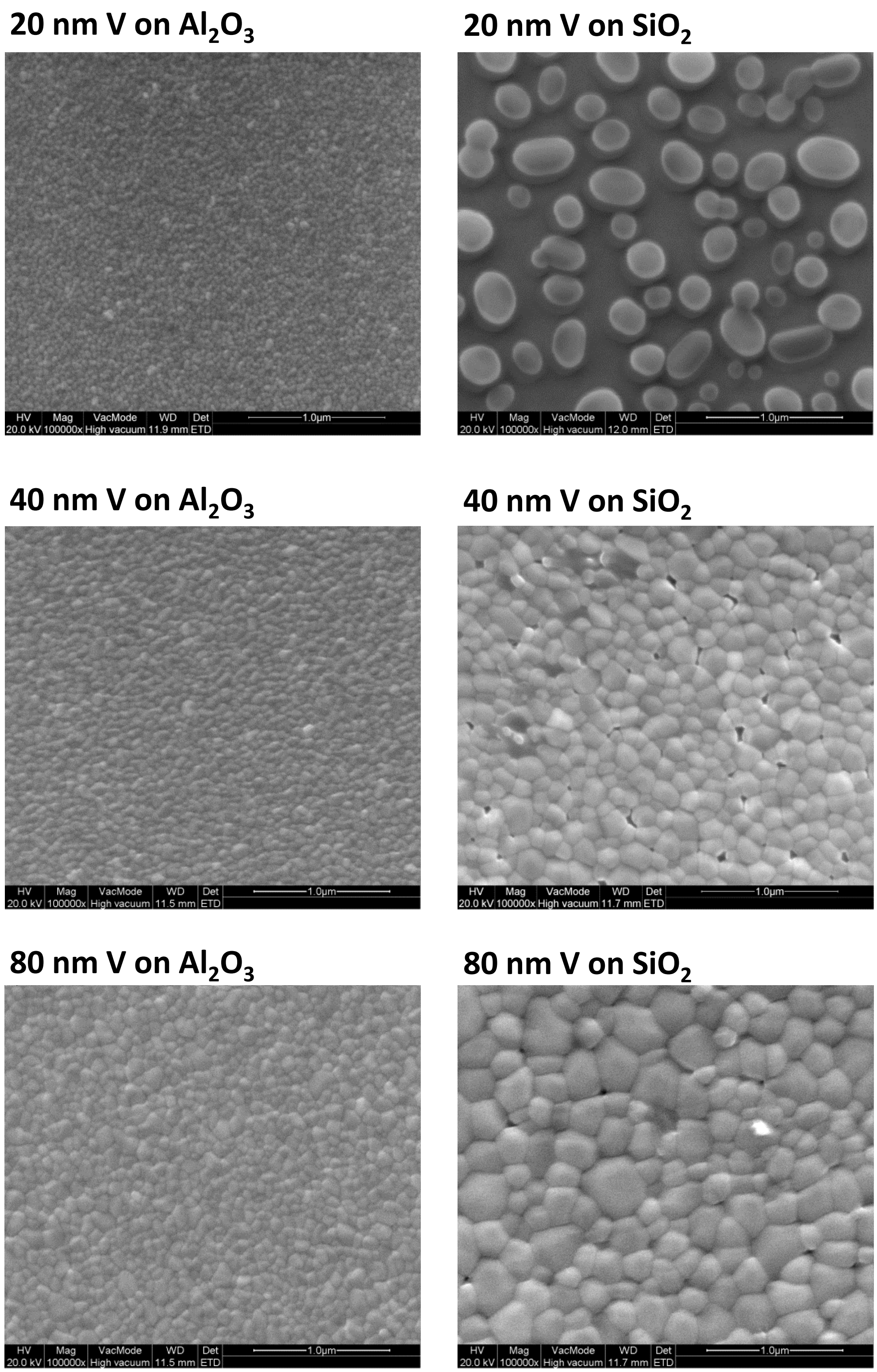

Fig. 3 SEM images of the films annealed at 480 °C in 0.2 mbar O_2.

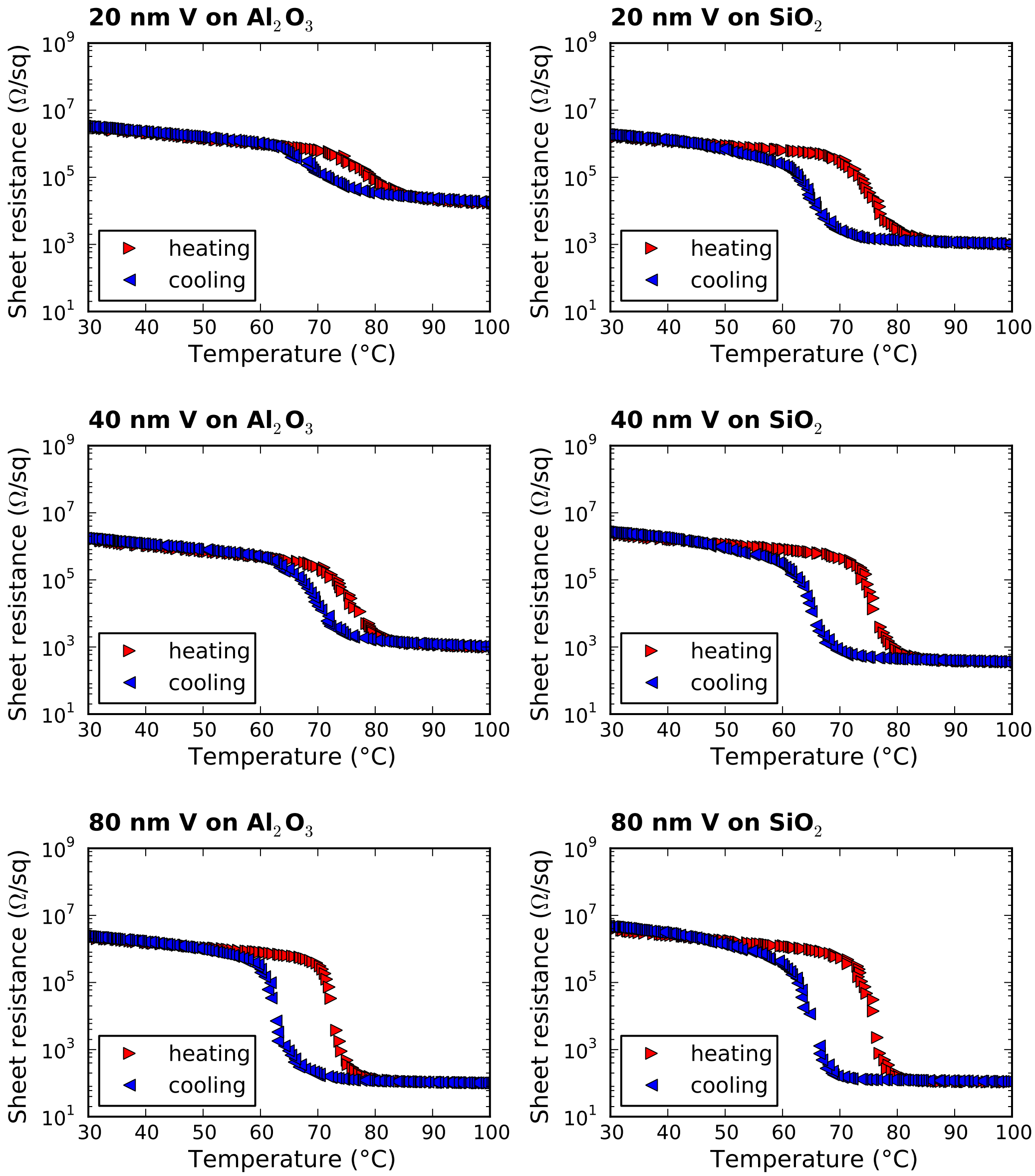

Fig. 4 Temperature dependent sheet resistance measurements after isothermal oxidation of 20 nm, 40 nm and 80 nm vanadium layers on the Al_2O_3 and SiO_2 templates at 480°C in a mixture of 50 mbar H_2 and 2 mbar O_2.

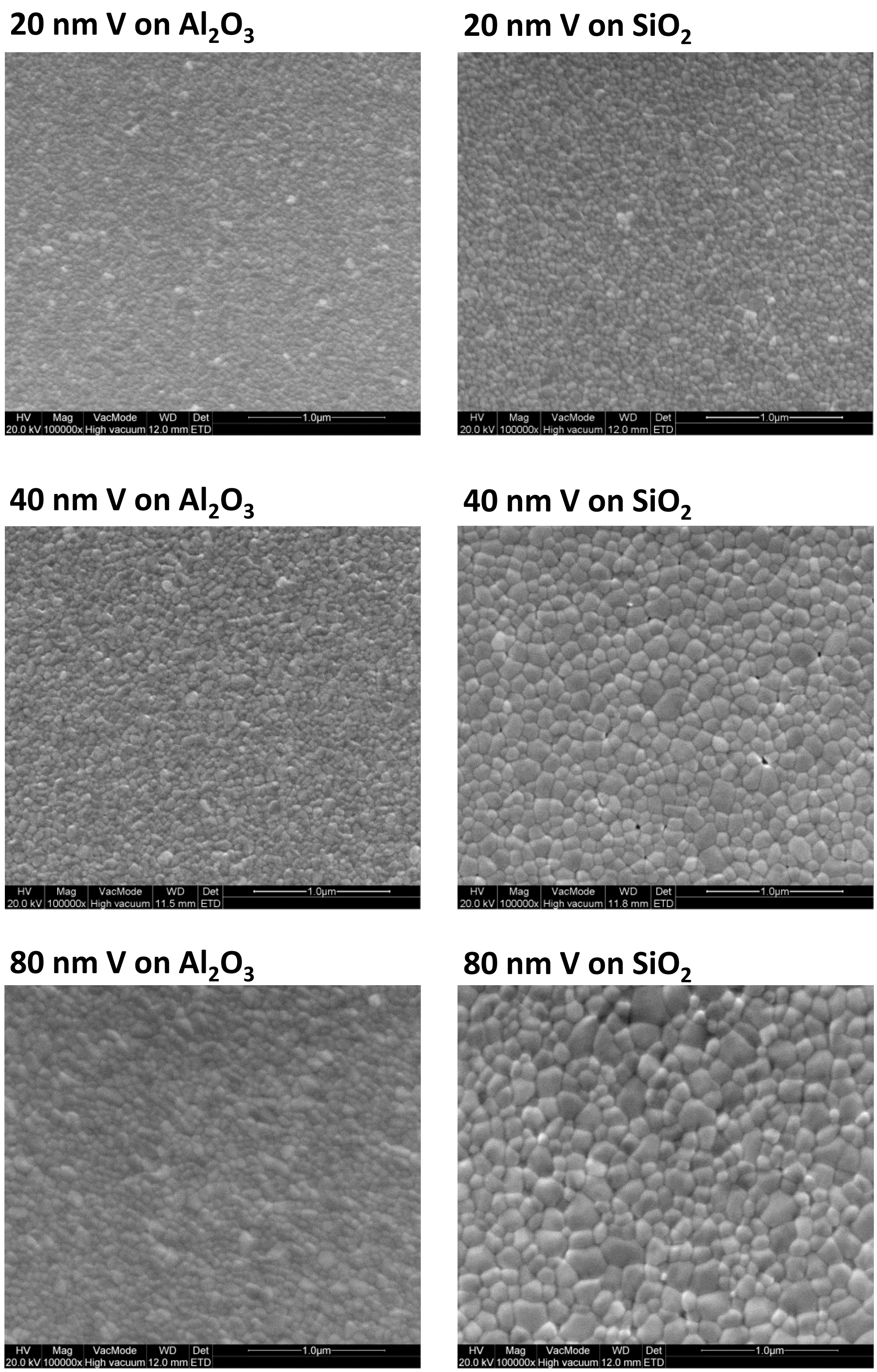

Fig. 5 SEM images of the films annealed at 480 °C in a mixture of 50 mbar H_2 and 2 mbar O_2.

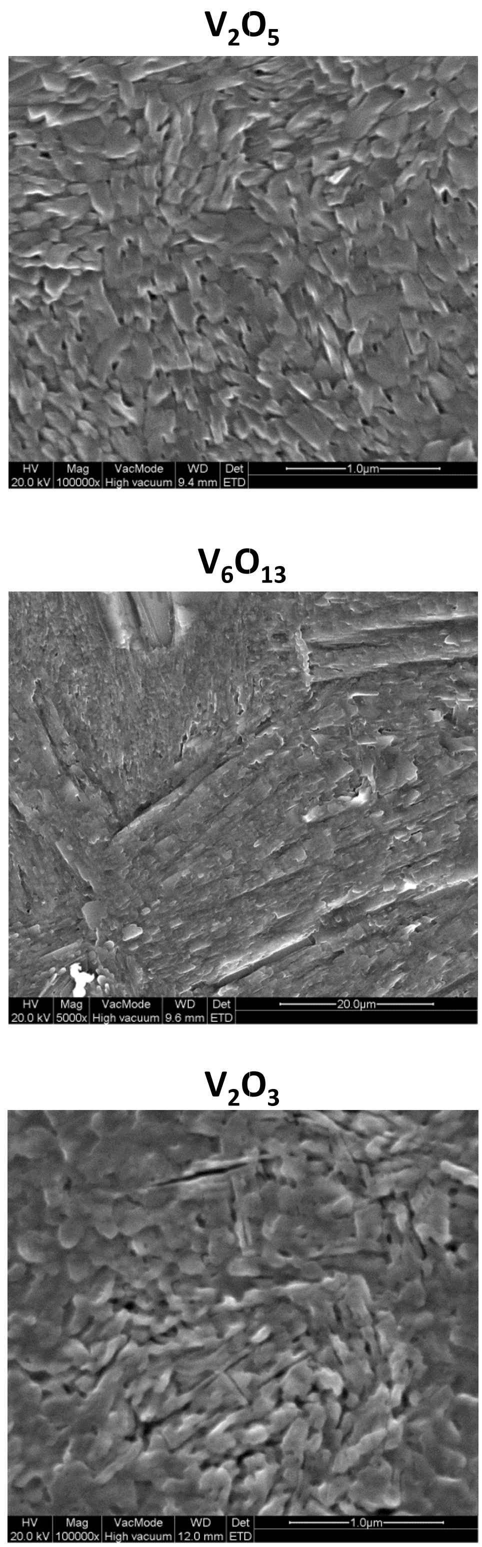

Fig. 6 SEM images of the V_2O_5, V_6O_{13} and V_2O_3 thin films.