Semiconductor-Metal Transition in thin VO_2 films deposited by ozone based Atomic Layer Deposition

Geert Rampelberg[a,*], Marc Schaekers[b], Koen Martens[b], Qi Xie[a], Davy Deduytsche[a], Bob De Schutter[a], Nicolas Blasco[c], Jorge Kittl[b], Christophe Detavernier[a]

[a] *Ghent University, Krijgslaan 281 (S1), 9000 Ghent, Belgium*
[b] *IMEC, Kapeldreef 75, B-3001 Leuven, Belgium*
[c] *Air Liquide Electronics, Tour Tupka C – 14 rue Hoche, 92039, Paris La Défense, France*

In the large group of vanadium oxides a lot of phases exist which undergo a semiconductor-metal transition (SMT). Vanadium dioxide (VO_2) has attracted the most attention since its transition temperature is at 68°C.[1] Below this temperature it has the semiconducting monoclinic structure, while it transforms to the metallic tetragonal structure when it is heated above this temperature. A change in resistivity up to 5 orders of magnitude occurs in a very small temperature range, which could be very interesting for applications in microelectronics, including resistive switches and memories.[2] Due to aggressive scaling and increasing integration complexity, atomic layer deposition (ALD) is gaining importance in microelectronics. However, attempts to grow VO_2 by ALD result in most cases in the undesirable V_2O_5.

In this work, we demonstrate the successful growth of VO_2 thin films by using Tetrakis[EthylMethylAmino]Vanadium and ozone in an ALD process at only 150°C.[3] As a substrate Si wafers with a thermally grown SiO_2 layer were used. A linear growth as a function of the number of ALD cycles was observed, indicating a growth of 0.7Å per cycle (Fig. 1). X-ray photoelectron spectroscopy (XPS) revealed a 4+ oxidation state for the vanadium in the case of this ozone based process, related to VO_2 (Fig. 2a). On the other hand, a 5+ oxidation state has been observed for ALD films grown using oxygen plasma with long plasma exposures, corresponding to V_2O_5 (Fig. 2b). From x-ray diffraction (XRD) it appeared that the plasma-process resulted in crystalline V_2O_5, confirming the XPS result, while for the ozone based process the films were still amorphous. In-situ XRD during a thermal treatment in helium ambient at 450°C showed that such a film of 42nm crystallized into the tetragonal VO_2(R) phase (Fig. 3). The fitted peak intensity is also shown as a function of time. No other vanadium oxide phases have been observed.

In-situ XRD confirmed the reversible structural transition between the monoclinic (M1) and tetragonal (R) during thermal cycling of the annealed film of 42nm (Fig. 4a). The transition temperature lies near the expected value of 68°C, with a hysteresis of approximately 12°C. Correlated to the structural transition, the electronic transition has been observed by two-point resistivity measurements in the same setup (Fig. 4b). The resistivity varied over more than 2 orders of magnitude and appeared to have a similar hysteresis.

References

1. F. J. Morin, Phys. Rev. Lett. **3**, 1 (1959).
2. M. J. Lee, Y. Park, D. S. Suh, E. H. Lee, S. Seo, D. C. Kim, R. Jung, B. S. Kang, S. E. Ahn, C. B. Lee, D. H. Seo, Y. K. Cha, I. K. Yoo, J. S. Soo Kim and B. H. Park, Adv. Mater. **19**, 3919-3923 (2007).
3. G. Rampelberg, M. Schaekers, K. Martens, Q. Xie, D. Deduytsche, B. De Schutter, N. Blasco, J. Kittl, C. Detavernier, Appl. Phys. Lett. **98**, 162902 (2011).

[*] *corresponding author e-mail:* geert.rampelberg@ugent.be

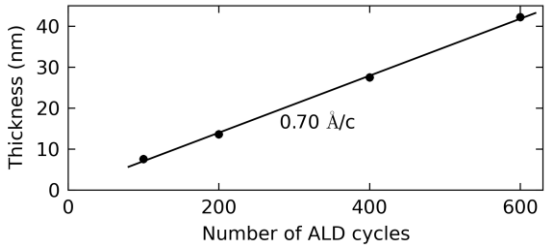

Fig. 1: Film thickness as a function of the number of ALD cycles. A growth rate of 0.7Å per cycle is extracted.

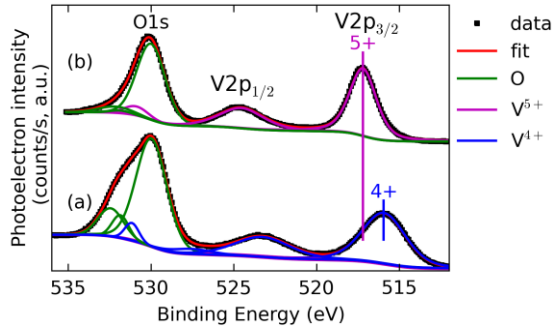

Fig. 2: X-ray photoelectron spectra at the surface of (a) an ALD film grown with ozone, and (b) an ALD film grown by using oxygen plasma. The ozone based process resulted in V^{4+}, related to VO_2, while the plasma grown film appeared to have the V^{5+} state, i.e. V_2O_5.

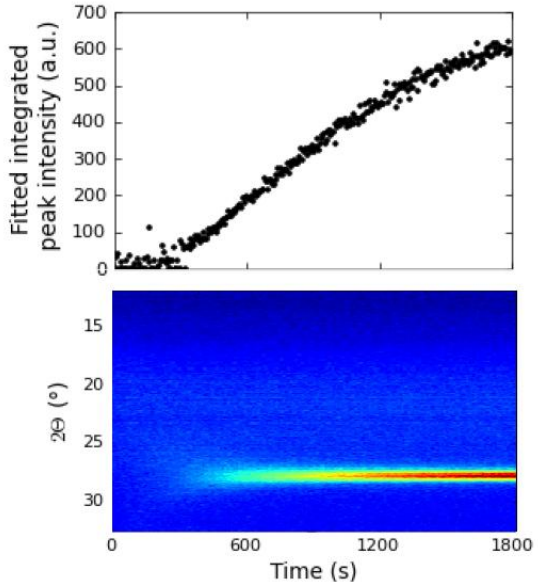

Fig. 3: In-situ XRD during thermal annealing of a 42nm ALD film in He at 450°C shows the formation of the VO2 (R) phase. The fitted peak intensity is also shown as a function of time.

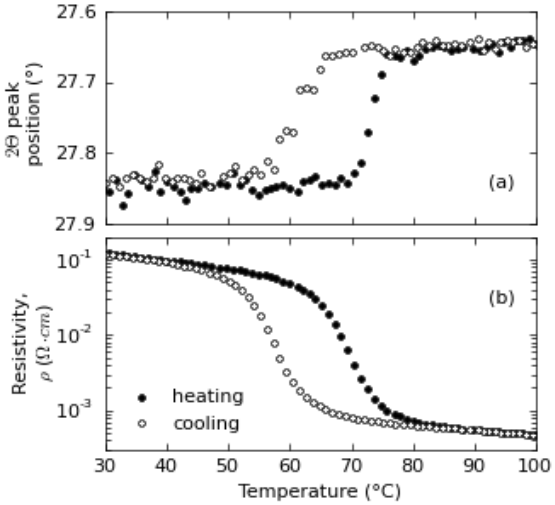

Fig. 4: Semiconductor-metal transition for a 42nm film annealed for 30 minutes at 450°C in He: (a) XRD shows the structural transition during thermal cycling between 30 and 100°C, from monoclinic (M1) to tetragonal (R), (b) resistivity varies up to two orders of magnitude.