Semiconductor-metal transition in thin VO_2 films grown by ozone based atomic layer deposition

Geert Rampelberg[1], Marc Schaekers[2], Koen Martens[2], Qi Xie[1], Davy Deduytsche[1], Bob De Schutter[1],
Nicolas Blasco[3], Jorge Kittl[2], Christophe Detavernier[1]

[1] Department of Solid State Sciences, Ghent University, Krijgslaan 281/S1, B-9000 Ghent, Belgium
[2] IMEC, Kapeldreef 75, B-3001 Leuven, Belgium
[3] Air Liquide Electronics, Tour Kupka C - 14 rue Hoche, 92039, Paris La défense, France
Geert.RampelbergUGent.be

Vanadium dioxide (VO_2) has the interesting feature that it undergoes a reversible semiconductor-metal transition (SMT) when the temperature is varied near its transition temperature at 68°C.[1] The variation in optical constants makes VO_2 useful as a coating material for e.g. thermochromic windows,[2] while the associated change in resistivity could be interesting for applications in microelectronics, e.g. for resistive switches and memories.[3] Due to aggressive scaling and increasing integration complexity, atomic layer deposition (ALD) is gaining importance for depositing oxides in microelectronics. However, attempts to deposit VO_2 by ALD result in most cases in the undesirable V_2O_5.

In the present work, we demonstrate the growth of VO_2 by using Tetrakis[EthylMethylAmino]Vanadium and ozone in an ALD process at only 150°C. XPS reveals a 4+ oxidation state for the vanadium, related to VO_2. Films deposited on SiO_2 are amorphous, but during a thermal treatment in inert gas at 450°C VO_2(R) is formed as the first and only crystalline phase. The semiconductor-metal transition has been observed both with in-situ X-ray diffraction and resistivity measurements. Near a temperature of 67°C, the crystal structure changes from VO_2(M1) below the transition temperature to VO_2(R) above with a hysteresis of 12°C. Correlated to this phase change, the resistivity varies over more than 2 orders of magnitude.

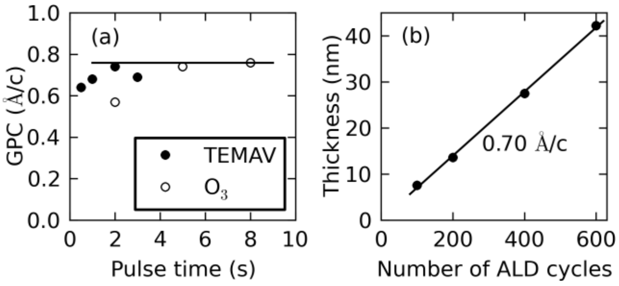

Fig. 1. ALD characteristics for the process TEMAV – O_3 at 150°C: (a) Growth per cycle versus exposure times for TEMAV with a fixed O_3 exposure of 5s (filled symbols) and for O_3 with a fixed TEMAV exposure of 2s (open symbols); (b) Thickness of the deposited films as a function of the number of ALD cycles.

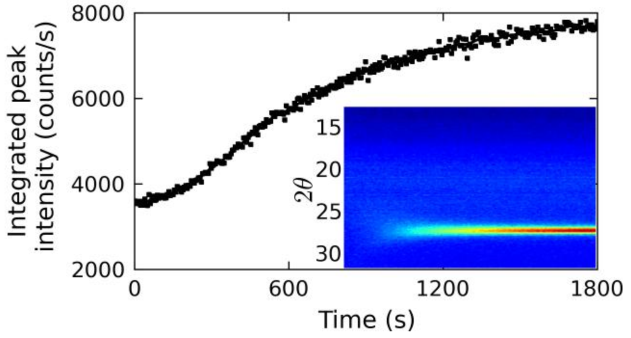

Fig. 2. Integrated intensity for the diffraction peak of the VO_2(R) 110 plane during an isothermal anneal of 30 minutes at 450°C in He for a film of 42nm. The inset shows the in-situ XRD measurement from which the peak intensity was integrated.

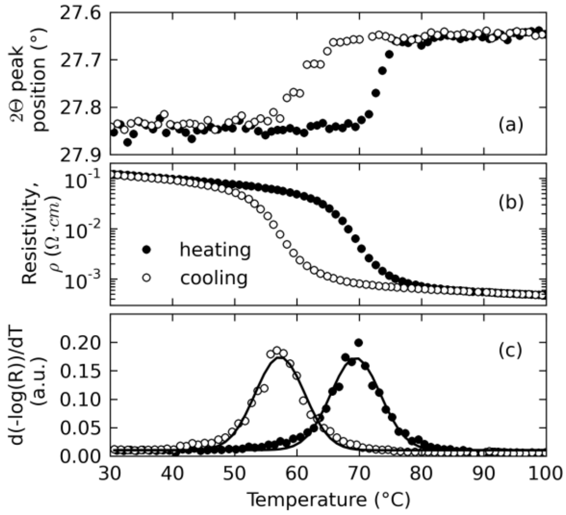

Fig. 3. Semiconductor-metal transition as observed during a thermal cycle between 30 and 100°C, with fixed heating and cooling rate of 0.1°C/s: (a) in-situ XRD, showing the change in crystal structure, (b) the correlated change in resistivity, and (c) a Gaussian curve fit to d(-log(R))/dT for the analysis of the resistivity.

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