

Optimization of the annealing conditions for thin VO₂ ALD films

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Vanadium dioxide (VO₂) is an intriguing material due to its semiconductor-metal transition (SMT). During this transition, which occurs near 67°C, electrical as well as optical properties change drastically. Possible applications include thermochromic windows, and memories or switches in micro- and optoelectronics. Although atomic layer deposition (ALD) is gaining importance for some of these applications, the growth of VO₂ with this technique is not obvious, since in most cases V₂O₅ is obtained.

In our previous work we presented ALD growth of VO₂ by using Tetrakis[EthylMethylAmino]Vanadium and ozone at a temperature of 150°C [1]. XPS revealed the 4+ oxidation state of vanadium, indicating growth of VO₂. Post-ALD thermal processing proved essential to crystallize the VO₂ in the desired tetragonal phase (R). In this work we present the influence of the oxygen partial pressure on phase formation during such thermal processes. Additionally the influence of film thickness and annealing temperature on the post-annealing properties were studied, including morphology and SMT characteristics.

During thermal processing a minimum oxygen partial pressure of approximately 1 Pa is indispensable to form crystalline VO₂ (R) (figure 1). Oxygen partial pressures above 2 Pa show an intermediate monoclinic phase (B), which transforms to VO₂ (R) at higher temperatures. At a value of 35 Pa this VO₂ (B) phase finally transforms to V₆O₁₃ instead of VO₂ (R). For very thin films, the thermal post-processing may result in agglomeration of the VO₂ layers on the SiO₂ substrate. Samples with a film thickness above 20nm show a typical resistivity ratio during the SMT of more than 2 orders of magnitude when annealed in the range 450°C to 500°C. For thinner films or higher annealing temperatures the resistivity ratio is suppressed and an overall increased resistivity is observed due to agglomeration (figure 2).

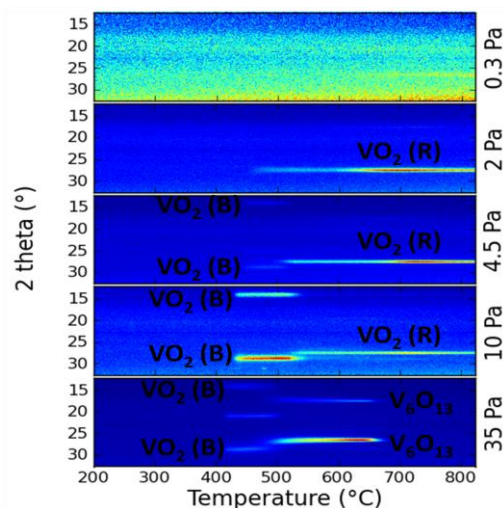


Figure 1: In-situ XRD during thermal annealing in varying oxygen partial pressure, showing crystallization of amorphous VO₂ ALD films.

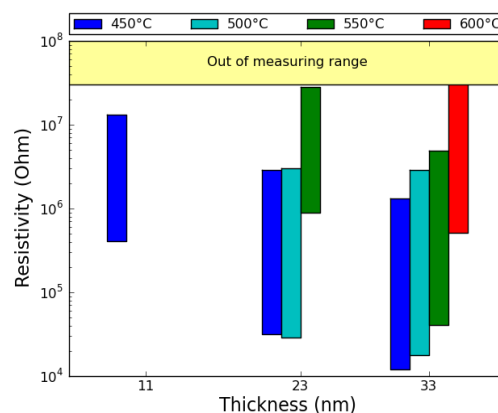


Figure 2: Resistivity change during the SMT for films of varying thickness, annealed to various temperatures. The top of the bars displays the resistivity at 40°C (i.e. where the VO₂ film is an insulator), the bottom shows the value at 100°C (where the VO₂ film has metallic properties).