

Proposal Code MA-2711

Proposal Title In situ crystallisation of (doped) VO₂ phases and investigation of the thermochromically active metal-to-insulator transition

Proposal Summary

This work will shed light into the formation mechanism of several vanadium dioxide (VO₂) phases. VO₂ is one of the most promising thermochromic materials and a target compound in a growing number of publications in materials science, chemistry and physics. A detailed understanding of the phase transitions of VO₂ is essential to establish the appropriate thermodynamic conditions that would reliably tailor an efficient thermochromic VO₂-based material. This proposal aims to investigate four key subjects in the state-of-the-art research on VO₂ phases: (1) the formation and crystallisation of monoclinic VO₂(B) phase; (2) the transformation of VO₂(B) into monoclinic VO₂(M); (3) the first order Metal-to-Semiconductor Transition (MST) from monoclinic VO₂(M) to rutile (tetragonal) VO₂; and (4) the influence of metal doping in the MST temperature and the interaction of metal dopants and vanadium atoms in doped VO₂(M) films. None of these transformations have been studied using combined *in-situ* characterisation techniques. To the best of our knowledge, this proposal will be the first comprehensive study of relevant VO₂ transitions for thermochromic applications using XAS, high resolution XRD (HRXRD) and Raman spectroscopy *in situ* under variable temperature conditions. Likewise, the impact of metal dopants in the VO₂ structure and their influence in the change of optical and electronic properties has not been elucidated.

Studies completed

Annealing of VO₂(B) phase under inert atmosphere: Samples of VO₂(B) were pressed into pellets and the change in crystal structure was observed on heating the samples to 550 °C and back to room temperature. Samples were monitored by both HRXRD and XANS/EXAFS. The XRD analysis showed a change from the (B) to (M) phases. Figure 1 shows the XANS and EXAFS analysis of the VO₂ powder. As shown, there was little change in the edge jump position, suggesting that the vanadium was remaining in the 4+ oxidation state, as expected when annealing in an inert atmosphere. The local coordination environment, Figure 1 (b), showed a substantial change with a large change in the local coordination when going from the (B) to (M) phases.

Two different VO₂ powders were used to study the (B) to (M) phase change- these samples displayed different local coordination environments. These samples also showed a difference in the rate of the phase change from (B) to (M) under the annealing conditions used. This was a surprising find and further investigations will be required to elucidate the reasons for the differences observed for these phase transitions.

A further series of experiments were conducted using VO₂ thin films- these were to study the composition of the films, deposited by chemical vapour deposition, as well as to study the

effect of dopants incorporated into these films. Figure 2 shows a typical edge-jump and XANS spectrum for an undoped VO₂ thin film. The data was modelled against V₂O₃ (V³⁺), VO₂ (V⁴⁺) and V₂O₅ (V⁵⁺); the films showed no evidence of V³⁺, but as shown had a mixture of V⁴⁺ and V⁵⁺ as evident from the edge-jump. Doped films were also measured, however the quality of the data collected was insufficient to clearly establish how the dopant type and concentration affected the local coordination environment.

Further studies are required on the thin film samples to establish a relationship between the oxidation state of the vanadium and how this affects the thermochromism and also the effect of dopants on both the oxidation of the bulk vanadium as well as changes to the local coordination environment. These studies will help establish design rules for synthetic routes towards optimised thermochromic thin films as well as give fundamental understanding of the role of dopants on the metal to semiconductor transition (MST).

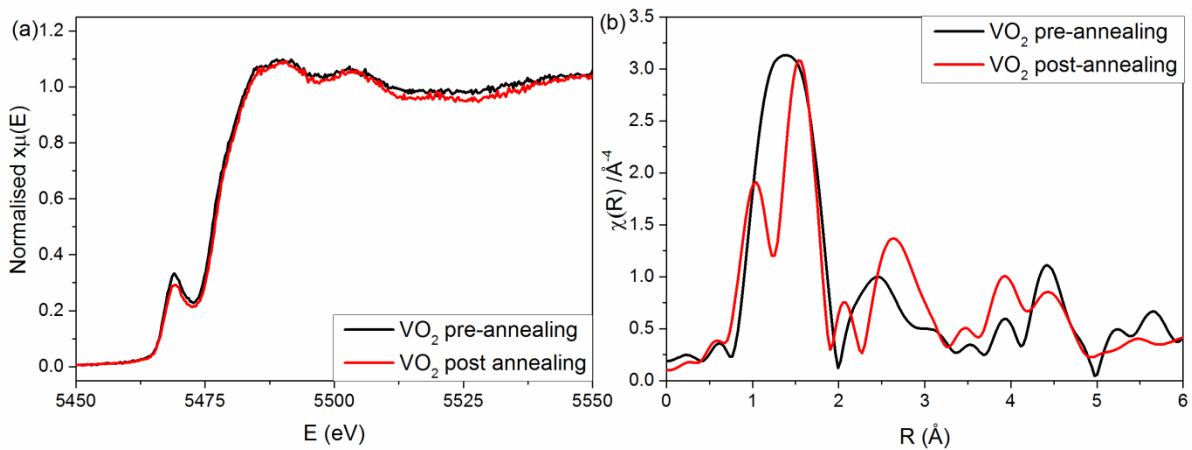


Figure 1: (a) XANS data showing edge jump for VO₂ samples; (b) R space showing local coordination environment for pre and post-annealed VO₂ samples.

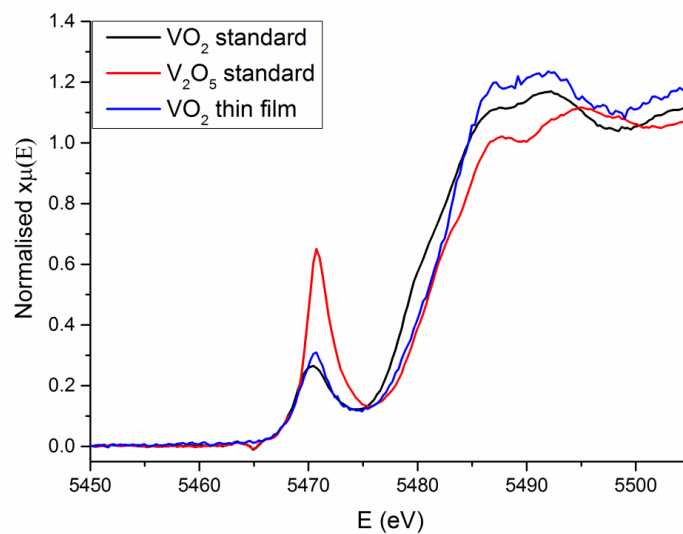


Figure 2: XANS data for VO₂ thin film on glass compared to VO₂ and V₂O₅ standards.