The University Of Sheffield.

E-Futures

# Mini-project report

# Further Investigation into the Thermochromism of Vanadium Dioxide Thin Films

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# ASSIGNMENT COVER SHEET 2010/2011

A completed copy of this sheet MUST be attached to coursework contributing towards theme 2 assessment.

| | |
|---|---|
| **Name :** | **Ben Crozier** |
| **Degree Course:** | **E-Futures DTC** |
| **Supervisor:** | **Prof Merlyne De Souza** |
| **Signature:** | |

I declare that this work is my own and that I have made appropriate reference to any sources used. I am aware of the handbook section on 'Plagiarism' and declare that this work is consistent with those guidelines.

Ben Crozier

**Mini-Project Mark Sheet**

**Student:** **Grade:** fail/satisfactory/good/very-good/excellent

**Supervisor:**

**Feedback:**

| | Excellent | Good | Average | Poor | Very Poor | Not Done | Not applicable |
|---|---|---|---|---|---|---|---|
| Introduction to the problem / subject | | | | | | | |
| Statement of aims | | | | | | | |
| Experimental description | | | | | | | |
| Presentation of results / findings | | | | | | | |
| Quality and depth of discussion / interpretation | | | | | | | |
| Relevance of conclusions | | | | | | | |
| Quality of English | | | | | | | |
| Use of reference material | | | | | | | |
| Evidence of external reading | | | | | | | |
| Quality of presentation | | | | | | | |
| Use of figures | | | | | | | |

**Comments**:

**Further Investigation into the Thermochromism of Vanadium Dioxide Thin Films**

## 1. Introduction

The financial cost of heating the home is ever increasing. In addition to this, the continued use of fossil fuels are jeopardising the worldwide climate. This practise is non-sustainable and must be remedied to provide a healthy and economically stable environment. An alternative to conventional heating is solar passive heating, which relies upon excellent insulation and air circulation to distribute air warmed by the sun through the home.

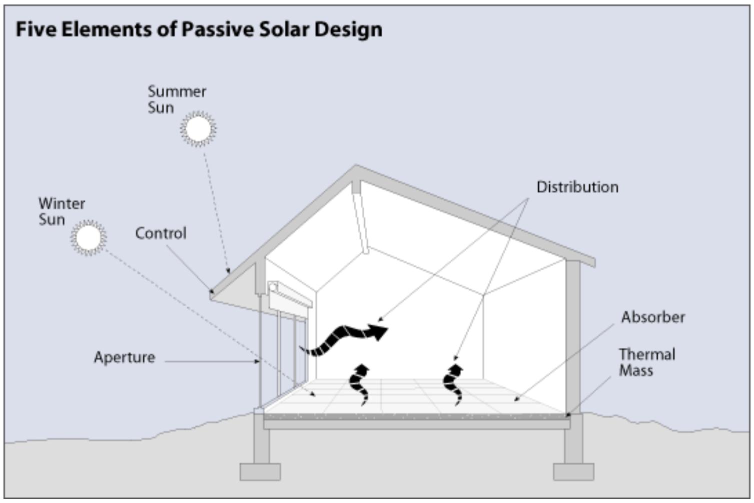


**Figure 1 – Description of Solar Passive Heating.** [1]

Chromic materials can be combined with solar passive heating to further enhance the advantages. [2] Chromic materials change their colour with stimulus, most common being electricity (electrochromic) or temperature (thermochromic). Chromic windows would change colour under stimuli, blocking out sunlight from the home when the internal temperature was comfortable, thus preventing the building from becoming too hot. Most notable of the thermochromic materials is vanadium dioxide, due to its low transition temperature of approximately 68$^{o}$C. [3]

## 2. Previous Work

The first steps were to optimise the deposition conditions using an RF sputtering system combined with a precursor oxidation process. [4] The conditions were modified in order to produce a film with a thickness of approximately 50 nm, whilst ensuring that the RF power and general energy costs were minimised. The conditions found to be most suitable were an RF power of 40W with a deposition time of 40 minutes. The films were annealed for 4 hours, at three different temperatures; 390$^{o}$C, 400$^{o}$C and 410$^{0}$C. It was important that the film was of high purity vanadium dioxide ($VO_2$), so Raman spectroscopy was used to evaluate the film's composition.

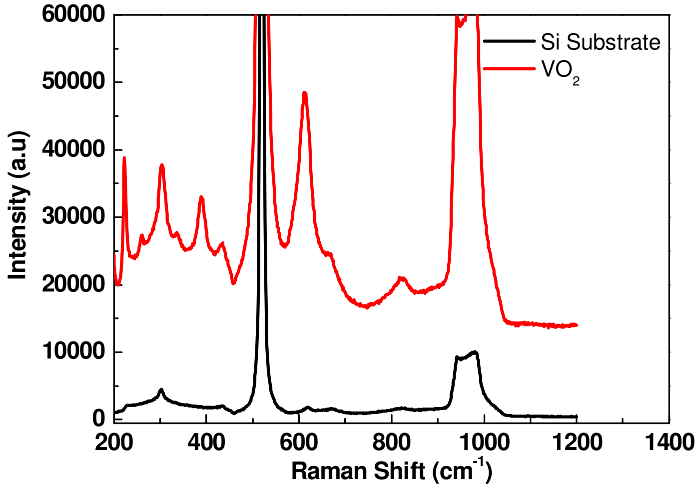


**Figure 2 – Raman spectra of $VO_2$ thin film.**

The Raman spectra confirmed that the film was high purity $VO_2$ [5], with no formation of vanadium pentoxide ($V_2O_5$). The species in particular must be minimised as it can cause health problems, as well as increasing the transition temperature of the film.

The aims of this mini project were to analyse the films created previously in much more detail, and evaluate whether they agreed with the literature. The resistance and reflectance must be recorded and improvements should be made based on these results.

## 3. Method

The resistance measurements were taken using a cryo-probe station interfaced with a Keithley 4200 meter. Photoresist layer spin coated onto the films and partially exposed to UV radiation. Once developed, the exposed photoresist was removed from the wafer. Aluminium deposited onto the patterned films using a mask aligner. Photoresist removed leaving patterned aluminium contacts. Resistance measured at room temperature and approximately 70°C. Reflectance measurements attempted using a BTC 261E cooled InGaAs array spectrometer. Films deposited onto glass substrates using previously optimised conditions of 40W RF power for 40 minutes. Films annealed at 390°C, 400°C and 410°C. Reflectance measurements recorded at room temperature and after heating using a hot plate.

## 4. Results and Discussion

The resistance of the films were studied as a function of temperature. It is well known that when $VO_2$ thin films are heated above the transition temperature their resistance drops sharply. [6] The meter scans over a voltage range and measures the current through the film. The resistance is easily calculated from a graph of current versus voltage.

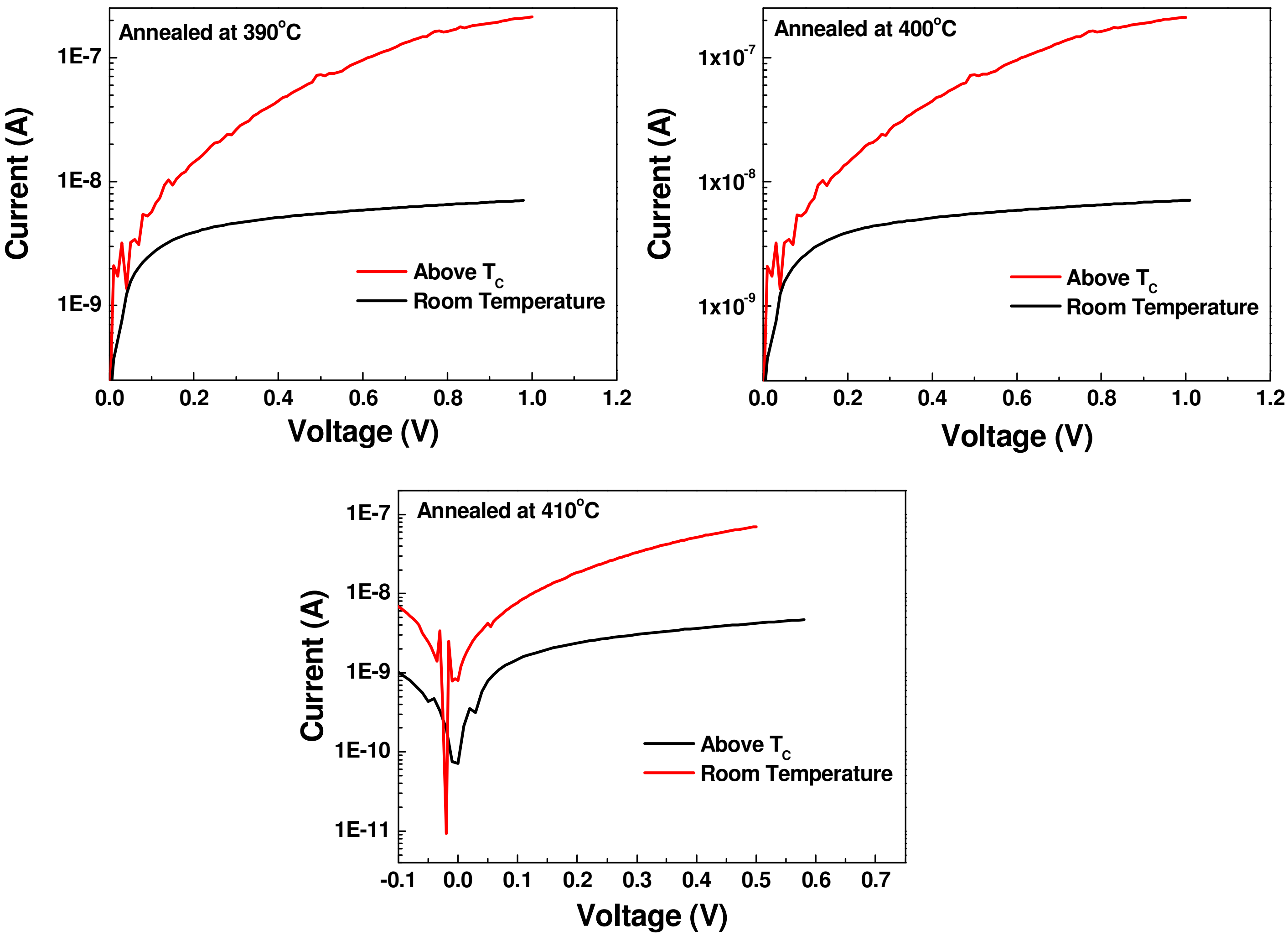


**Figure 3 – Graphs illustrating the drop in resistance above the critical temperature ($T_C$) of 68°C.**

At room temperature all three films showed resistance in the mega-ohm region. Once heated to roughly 345K the resistance of the films fell dramatically, with the maximum reduction being that of the film annealed at 400°C, showing a high temperature resistance 14 times lower than the resistance recorded at room temperature.

| Annealing Temperature/ °C | 390 | 400 | 410 |
|---|---|---|---|
| Room Temperature Resistance/ Ω | $17.3 \times 10^6$ | $127 \times 10^6$ | $159 \times 10^6$ |
| High Temperature Resistance/ Ω | $1.69 \times 10^6$ | $9.04 \times 10^6$ | $21.0 \times 10^6$ |

**Table 1 – Comparison of high and low temperature resistance values with respect to increasing annealing temperature.**

It was also noted that as the annealing temperature increased, the resistance increased. This was probably due to the higher temperature oxidations resulting in the formation of more oxide material, which is the cause of the resistance within the film.

Reflectivity measurements were attempted in order to evaluate how the film's transparency changes with temperature. It was predicted that above the transition temperature (approximately 68°C) the reflectance of the film was increase significantly. [7] However, this was not the case and the reflectance increased only slightly. The probable reason behind this was that the opaque silicon substrate prevented accurate measurements. For this reason depositions at 390, 400 and 410°C were performed using glass as a substrate. As the ultimate objective is to create a "smart window", the use of glass as a transparent substrate was a logical step. However, the changes were again minimal.

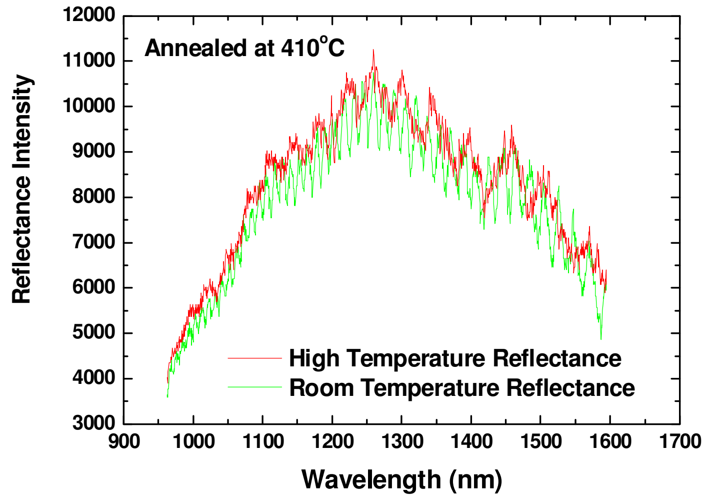


**Figure 4 – Reflectance graph showing minimal change in reflectance intensity, as well as unexplained oscillations.**

The probable reason behind the poor results was that the apparatus was crude, and the film temperature was not known. The samples have been sent to a research associate in Germany for further analysis, using more specialised equipment. Although the measurements were unsuccessful, they did show some interesting results. As seen on the graph above, the reflectance curves show periodic oscillations, the cause of which are as yet unknown.

## 4. Conclusions

The significant drop in resistance seen during the resistance measurements, combined with the Raman data, showed that the films were composed of vanadium dioxide. The resistance data agreed strongly with the literature and was an encouraging result. The reflectance data was the opposite. When above the transition temperature, $VO_2$ films will have a much higher reflectance due to the colour change that accompanies the transition. The problem with the measurements was that the temperature was unknown, meaning it was not definite that the films were above 68$^{o}$C. It is hoped that the results from Germany will be different, and more in line with the previous findings of the investigation. However the reflectance measurements did yield one interesting result; the oscillations observed in the data. This requires further investigation to reveal its causes, which could be fascinating.

## 5. Future Work

The next step of the investigation is to obtain accurate values for the transition temperature for all three films. This can be accomplished again using the cryo-probe system, gradually increasing the temperature of the film whilst looking for dramatic resistance changes. It is also important to get an accurate value of thickness for the films; which would allow the calculation of their resistivity. It would be interesting to observe how the resistance values for the films deposited onto glass substrates differ from those on silicon. Finally, doped samples must be attempted to bring these properties towards applications in the home.

## 6. References

1. http://www.iklimnet.com/save/passive_solar_heating.html
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