Temperature dependence of optical and transport properties in VO_2 with high temperature anomalies

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Abstract

Thermochromic VO_2 is of interest for energy efficient glazing, and for fast telecommunications because it optically switches in the near IR. Despite extensive study several aspects of its apparently diverse behaviour have not been explained satisfactorily. The visible-NIR permittivity and dc electrical conductivity of high quality thin films of VO_2, across the metal-insulator phase transition and well into the metallic phase to temperatures up to 100°C above Tc are studied as a function of temperature and grain size. Experimental behaviour is partly explained with effective medium models, existing band structures and classical transport theory. Anomalies however include: unphysically fast relaxation rate, counter-intuitive and significant differences between optical and dc, and bulk and thin film parameters; and residual "non-metallic" features above the transition in highly oriented films. Residual, but transient high temperature d-electron singlet pairing on V dimers, which is sensitive to nanostructure, is examined as a source of some anomalies.

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Keywords: vanadium dioxide, metal insulator transition, thin film, thermochromic

Introduction

Many oxide, sulphide and selenide compounds exhibit metal-insulator (MI) or metal-superconductor phase transitions [1]. Their metal phases occur above the transition temperature T_c and can display transport properties which do not obey fermi liquid theory. Such anomalies in the metal phase of VO_2 are the subject of this report. VO_2 is also technically important because its metal phase emerges above 68° C, and is accompanied by a drop in resistivity by up to 4 to 5 orders of magnitude. The infra red optical properties shift from a transmitting semiconductor phase to a reflecting Drude/plasmonic system. This optical transition can occur in femtoseconds in nanoparticles of VO_2 which is anomalously fast [2]. Such switching speeds indicate that electron-electron (e-e) interactions rather than phonon induced structural effects lead to the transition and that these e-e interactions occur at very high frequency. Persistence of strong e-e interactions in the metal phase will be indicated by our anomalous data on thin films in both the optical and dc regimes, with more anomalies observable in dc data. There has been occasional attention to one puzzling aspect of the metal phase properties in both dc and infra-red optical data, namely a carrier relaxation rate around 0.75 eV [3-5]. It implies an anomalous mean free path less than a lattice spacing, and has been attributed to sample problems [3], and to frequency dependence of relaxation rate [5], but evidence is mounting that neither explanations are correct [4, 6] and that this is the real quasi-particle relaxation rate. For further insights we present data on dc resistivity to temperatures well above T_c for films with two different grain sizes. They show non-metal like dc response despite their good plasmonic optical properties.

Experimental

VO_2 films were produced on both glass and mica substrates via the same method. The process involved DC Magnetron sputtering of Vanadium, followed by a controlled oxidation/annealing process, during which the substrate temperature was maintained at 450°C. The post deposition annealing was carried out for around 6 hours at a pressure of 0.1 Torr after slowly introducing air into the chamber. Various thickness films were produced from 20nm to 150nm, with the annealing time varied to suit. The films produced on a glass substrate had a grain size of approximately 50nm while the mica substrate produced 100nm grain size, as shown in the micrographs of figure 1.

Optical reflectance and transmittance measurements were carried out using a Cary 5E UV-VIS-IR Spectrophotometer utilising an in-house developed heating setup allowing measurements to be taken at temperatures from 25°C up to 150°C. The temperature was controllable such that optical hysteresis measurements could be made at 1°C intervals.

A computer controlled four wire resistance method was utilised to measure the sheet resistance hysteresis of the VO_2 films. Resistance and temperature data were acquired with 7552 Yokagawa digital multimeters, interfaced with the LabView program which controlled the temperature of the sample. A copper mask was deposited on top of the films to allow for attachment of the probes for resistance measurement.

Results and discussion

The change to plasmonic response in both films can be observed in the spectral transmittance and reflectance plots in figures 2 and 3. The oscillations in figure 2 are due to interference caused by the thickness of the mica substrate. Both the films produced on mica and glass had very similar optical constants for VO_2. Applying Drude fits to the long wavelength part of the metal phase data yields the plasma frequency (ω_p = 3.9eV) and relaxation frequency (ω_τ = 0.71eV). The relaxation frequencies are always anomalously high. It is in dc resistivity ρ that grain size dependent differences show up as in the hysteresis plots of figure 4. The magnitudes in $\Delta\rho$ at T_c are quite distinct. The 50nm grain size sample has $\Delta\rho$ of 2 orders of magnitude while the 100nm grain size sample has $\Delta\rho$ of 3 orders. Similar differences in $\Delta\rho$ with grain size have been seen [7] on sputtered films with grain size increasing from 50 nm to 350 nm. Thus while the optical transition is complete, the dc change is incomplete and grain size dependent. By contrast single crystal data [3] gives $\Delta\rho$ around 4 to 5 orders of magnitude.

The observations in reference [6] indicate e-e correlations in metallic VO_2 cause a shift in optical response with temperature only for field frequencies below 0.1 eV. In agreement we observed no significant difference in Drude parameters for T at 80°C and 140°C at frequencies just below 1 eV. The temperature dependence of resistance above Tc is anomalous and both grain size and thickness dependent. Grain size effect is stronger as shown by plotting ln ρ(T) versus 1/T in figure 5. This plot is not indicative of a metal, but indicates instead that conduction is thermally activated and continuing to rise as T is raised. The activation energies of 0.108 eV and 0.064 eV are significantly lower than

those of the semiconductor phase [4]. Films with similar grain size but varied thickness were found to have only small variations in activation energy. This activation energy is decreasing as grain size increases and when it vanishes for large enough grains we expect a shift to normal resistivity rising linearly with T as observed [3].

Conclusions

Summarising, it appears the incomplete $\Delta\rho$ transition and its associated "non-metal-like" activated conductivity are intrinsic to small enough grain sizes. The activation energy is strongly grain size dependent and weakly dependent also on film thickness. A stronger plasmonic response is found for small grains [4] but counter-intuitively this does not translate into a lower ρ value than that found in large grains and single crystals. The carrier relaxation frequency is apparently independent of grain size and always anomalously high.

These observations lead to the conclusion that e-e interactions are dominating the high T response and can lead to a very high relaxation rate at all frequencies below optical rates. A possible explanation of our thermally activated $\sigma(T)$ in nano-grains is that these fast e-e interactions also lead to size dependent transient pairing or quantum fluctuations [8]. Such transient pairing could open a transient pseudo-gap at the fermi surface [1], which can only be observed at low enough frequencies of the applied electric field. Transient coherence is a relatively new idea [8] with obvious technical potential. A theoretical framework beyond fermi liquid theory is needed to understand charge transport in such systems and VO_2 looks like a good candidate for such studies.

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Figure 1 – Scanning electron micrographs of a) 120nm of VO_2 on Mica - 100nm grain size b) 50nm of VO_2 on Glass - 50nm grain size.

Figure 2 - Transmittance of 120nm of VO_2 on a mica substrate, both above and below the semiconductor-metallic transition critical temperature, with Lorentz-Drude fit for the metallic phase. (100nm grain size)

Figure 3 - Reflectance and transmittance of 72nm of VO_2 on a glass substrate, both above and below the semiconductor-metallic transition critical temperature, including Lorentz-Drude fits for each. (50nm grain size)

Figure 4 - Resistivity Hysteresis for the 50nm and 100nm grain size VO_2 films.

Figure 5 – Ln ρ(T) versus 1/T with linear fits for activation energy for activation energy fits for 50nm and 100nm grain size VO_2 films.

Figure 1 - GENTLE

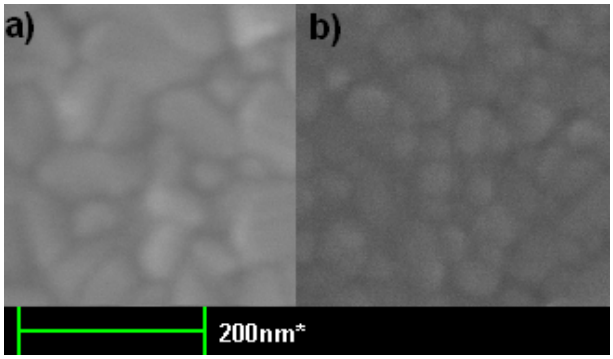

Figure 2 - GENTLE

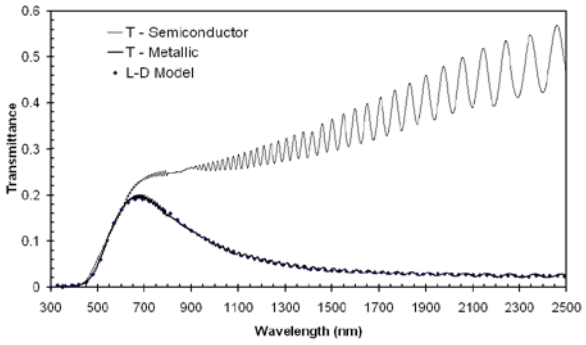

Figure 3 - GENTLE

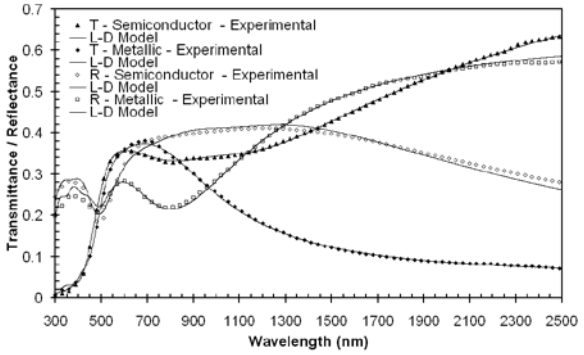

Figure 4 - GENTLE

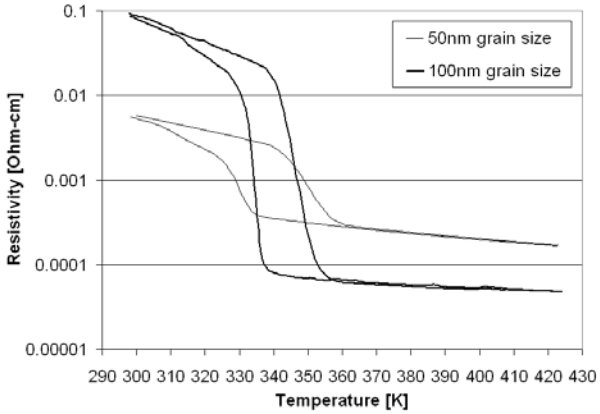

Figure 5 - GENTLE