Vanadium Oxides: Properties and Applications

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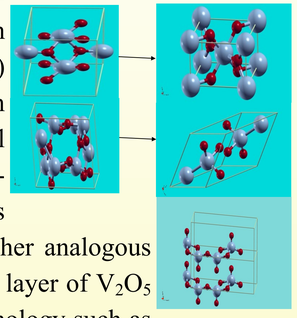
Introduction

In vanadium oxides, "correlated" electrons are responsible for extreme sensitivity of materials for small change in external stimuli such as pressure, temperature, or doping [1]. VO_2 is one of the widely studied materials which undergoes Insulator Metal Transition (IMT) at 340K; V_2O_3 and thin film of V_2O_5 show transitions at 160K and 530K respectively [2]. These phase transitions are reversible [3] and are accompanied by drastic change in crystallographic, magnetic, optical, electronic and electrical properties. VO_2 changes its structure from Monoclinic (I) to Rutile (M) (Top row); V_2O_3 from monoclinic (I) to Trigonal corundum (M) (second row); while IMT has been observed in the film (not in bulk) of V_2O_5 without structural change. Since graphene (single layer of graphite) exhibits interesting properties unlike its bulk counterpart, researchers are curious whether analogous interesting properties can be observed in single layer of V_2O_5 also! Vanadium oxides are widely used in technology such as memory devices, chromogenic materials, metamaterials, ultrafast switching, temperature sensors and thermal infrared (IR) detectors.



Computational Methods: ABINIT

ABINIT is a full ab-initio, free to use, simulation package based on Density Functional Theory (DFT), pseudopotentials (PPs) and Plane Waves (PWs). ABINIT mainly computes charge density, total energy and electronic structure of a periodic system, based on Kohn-Sham density functional approach, in an iterative way to obtain self-consistent solution.

Since pseudopotentials are used, core electrons are pre-calculated in an

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \sum_A Z_A \frac{e^2}{|\boldsymbol{r}-\boldsymbol{R_A}|} + e^2\int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' + U(\boldsymbol{r})\right]\phi_i = \varepsilon_i\phi_i$$

atomic environment and kept frozen during the calculation. Approximation to exchange-correlation used in the calculations is Local Density Approximation (LDA) with the functional of Perdew and Wang (PW92) [4]. We have an advantage of using LDA in our calculations in that they have the tendency of having smaller radii for their (PAW, Projector Augmented Wave) potential spheres which is consistent with relatively tightly packed vanadium oxides (VO_x: x=2 and 2.5) structures. Choice of valence bands is such that no "ghost" or "phantom" bands appear in the band structures. In oxygen, electrons in the first shell (n=1) are treated as core electrons while in vanadium, the electrons in first and second shell (n=2 and 3) are treated as core electrons.

Convergence test is done to truncate the plane wave expansion up to 40 Hartree [Ha]. Equidistance or Monkhorst-Pack (MP) grid is used to perform Brillouin Zone Sampling followed by convergence test for determining the density of k-mesh. Semi-classical transport coefficients are calculated by a tool, BoltzTraP (Boltzmann Transport Properties) [5], in a finer mesh by increasing k-point density.

Results and Discussion: Properties

V_2O_5: It is seen from Figure 1 that the bands are dispersive; Bands are relatively flat along Γ-X; Larger dispersion along Γ-Y and Γ-Z. This is a clear indication of anisotropic feature of the material. Band gap of 1.675 eV (Γ-T) is observed which is less than the reported value of 2.2 eV (LDA always underestimates band gap!). Figure 2 shows that the dominant thermoelectric carrier is hole in all directions a, b and c (Since S>0). Anisotropic behavior is indicated by all the transport coefficients.

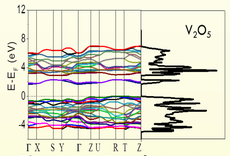


Figure –1 Band structure of bulk V_2O_5

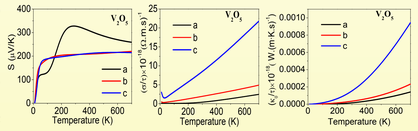


Figure –2 Transport coefficients of bulk V_2O_5

VO_2 (Rutile): Figure 3 shows the band structure of metallic phase of VO_2; clearly four groups of bands are observed. Transport Properties of VO_2 (M) near Fermi-Energy are calculated and presented in Figure 4. The electrical Conductivity is nearly anisotropic where as Seebeck coefficient and Thermal conductivity are clearly isotropic.

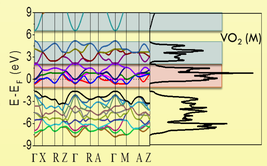


Figure –3 Band structure of bulk VO_2

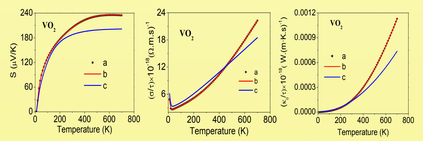


Figure –4 Transport coefficients of bulk VO_2 (M)

VO_2 (Monoclinic stable phase, M_1):

Figure 5 shows the band structure of insulating phase of VO_2;again four groups of bands are observed. Transport Properties of VO_2 (I) near Fermi energy are calculated and presented in Figure 6: no remarkable anisotropy in the Seebeck coefficient. "Kohn-Sham-Boltzmann" prediction of T_c for VO_2 is 332K (~340K [1]) as seen from Figure 7.

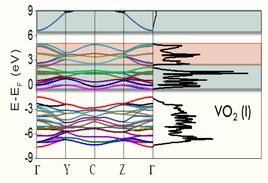


Figure –5 Band structure of bulk VO_2 (I)

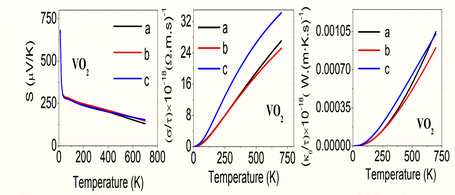


Figure –6 Transport coefficients of bulk VO_2 (I)

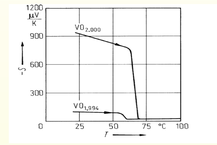
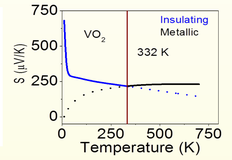


Figure –7 T_c of bulk VO_2: A "Kohn-Sham-Boltzmann" Prediction.



Results and Discussion: Applications

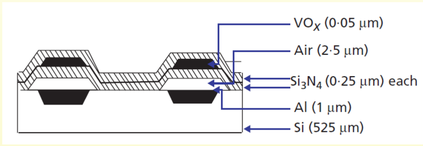
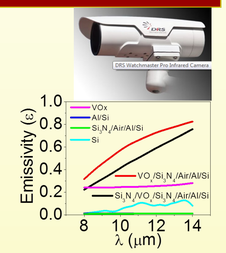


Figure 8 — Bolometer Structure, IR Camera, Emissivity



Room temperature spectral emissivity of an industry standard VO_x based bolometer structure, with x equal to 1.8, is presented [7]. Calculations show that the Si_3N_4 layer provides the much desired linear performance of the VO_x based bolometer.

Conclusions

V_2O_5 is highly anisotropic. VO_2 (M) is strictly isotropic in a and b directions. Phase transition temperature in VO_2 is 332 K: a "Kohn-Sham-Boltzmann" prediction! Silicon nitride layer plays a critical role to linearize the performance of the Honeywell microbolometer structure.

References

1. *G. Kotliar and D. Vollhardt "Strongly Correlated Materials: Insights from Dynamical Mean-Field Theory" Physics Today, 57, 53-59 (2004)*
2. *C. Lamsal and N. M. Ravindra "Optical Properties of Vanadium Oxides-An Analysis" Journal of Materials Science, 48, 6341-6351 (2013)*
3. *D.M. Lamb "Semiconductor to Metallic Phase Transitions from Vanadium and Titanium Oxides Induced by Visible Light" Missouri State University (2009)*
4. *J. P. Perdew and Y. Wang "Accurate and simple analytic representation of the electron-gas correlation energy" Physical Review B, 45, 13244-13249 (1992)*
5. *G. Madsen and D. Singh "BoltzTraP. A code for calculating band-structure dependent quantities" Computer Physics Communications, 175, 67-71 (2006)*
6. *W. Brückner, W. Moldenhauer, H. Wich, E. Wolf, H. Oppermann, U. Gerlach and W. Reichelt "The range of homogeneity of VO_2 and the influence of the composition on the physical properties. II. The change of the physical properties in the range of homogeneity" Physica Status Solidi (a), 29, 63-70 (1975)*
7. *C. Lamsal and N. M. Ravindra "Simulation of Spectral Emissivity of Vanadium Oxides (VO_x) Based Microbolometer Structures" Emerging Materials Research, 4, 194 -202 (2014)*