

THERMODYNAMIC STABILITY OF VO₂-METAL THIN FILMS

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DECLARATION

I declare that this dissertation hereby submitted to the University of Zululand for a degree of Master of Science has not been previously submitted by me for a degree at this or any other university, that it is my own work in design and execution, and that all material contained therein has been duly acknowledged.

.....

Signature

.....

Date

DEDICATION

This work is dedicated to my late Ma'Sbanyoni, my loving mother, if it were not for your undying love and faith I wouldn't have come this far. There is no doubt in my mind; you are the best mum I could ever ask for. I will always love and miss you!

.....*to my family.*

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ABSTRACT

Thermodynamic stability of VO₂ in contact with metals was conducted on solid thin metal films. The VO₂ film was synthesized on a corning glass under optimised condition parameters using rf magnetron reaction sputtering. The samples with structure glass/VO₂ were then taken for optical characterisation and the results obtained correlate well with theoretical behaviour of VO₂ thin film. UV-VIS-NIR Spectrometry was used to measure the optical behaviour of the VO₂ film. The structures on which a solid thin metal film of thermodynamic stability of VO₂ in contact with metals was conducted on solid thin metal films of Pd, Ni, Hf, Pt, Co, and Al were e-beam deposited on VO₂/glass. This resulted in structure of the form glass/VO₂/metal. The deposited samples were annealed in a furnace at different temperatures and time intervals keeping some of the as-deposited metals as virgin samples. Using Rutherford Backscattering Spectrometry (RBS), the samples were investigated if an interaction between VO₂ and metal has taken place by comparing the as-deposited (no heat) samples with annealed ones. RBS analysis was conducted using a 2 MeV beam of alpha particles. In case a reaction has taken place, X-Ray Diffraction (XRD) was used to identify the compound phases formed. The only metals found to show a reaction are Hf and Al when each was in contact with VO₂ and annealed. The metals (Pd, Ni, Pt, and Co) seem not to react with VO₂ at temperature up to 700°C annealed for one hour. For all the metals investigated heats of reaction were calculated for all the possible combinations. Our experimental observations were found to be in agreement with the theoretical predictions. In such cases ternary phase diagrams were constructed and found also to be in agreement with the experimental results. Metals with an average electronegativity less than 1.70 (the cross over point) in Pauling scale were found to react with VO₂ while those with average electronegativity greater than 1.70 were found not to react with VO₂. The Miedema electronegativity parameter was also used and metals whose values are less than the cross over point of 4.67 V were found to react while those metals greater than 4.67 V were found not to react. These predictions based on average electronegativity and Miedema electronegativity correlate well with our experimental results.

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CHAPTER 1

BACKGROUND AND SCOPE OF INVESTIGATION

1.1 Introduction

Materials technology has always a profound impact on the development of human societies. There is presently significant and growing demand for new materials with superior capabilities for sensing, actuating, and switching applications. The fundamental properties of this class of materials, along with their potential for applications have motivated a number of research and development efforts [1].

From the scientific and technology point of view, it is also interesting to study these materials at the nanometer length scale, either because their properties may be modified as a function of the particle size, or due to the particle interaction with surrounding matrix material, or both. Interest in metal nanoparticles has increased dramatically in recent years. Investigations into thin film metal-metal interaction could be approached from several perspectives. From a thin film point of view the interactions would be evaluated against the general behaviour of materials thin films.

1.1.1 VO₂ material: Brief introduction

Vanadium dioxide (VO₂) has attracted a lot of attention due to its importance in industrial applications such as laser protection, optical switches, and solar energy control for windows and space satellites. In this subsection properties of the VO₂ material are briefly introduced.

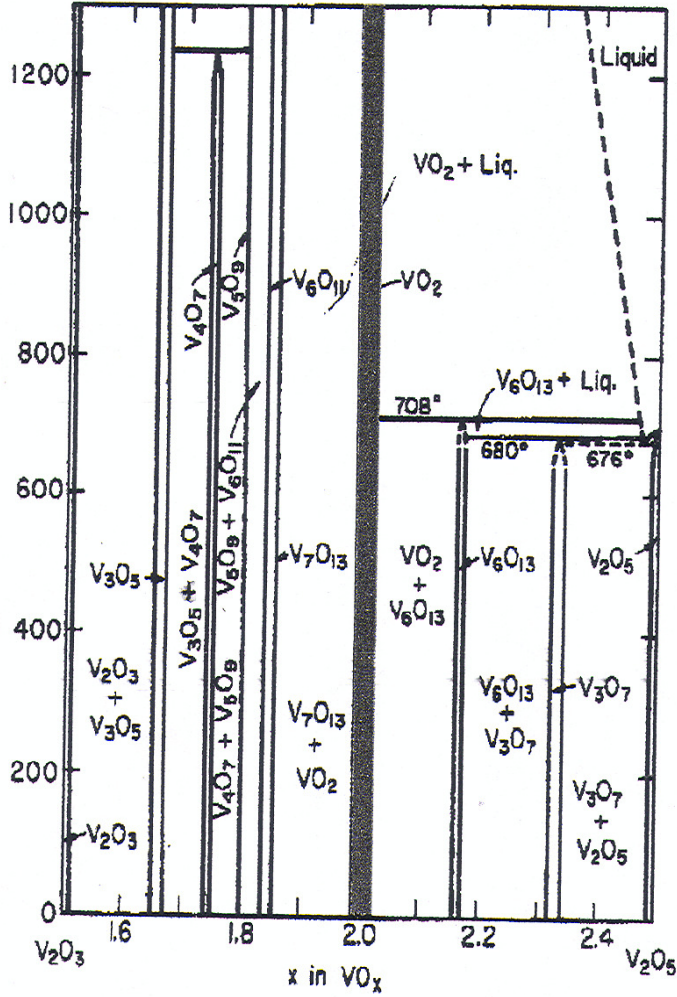
Vanadium is a transition metal with an atomic number 23 and atomic mass of 50.9414 g/mol. As vanadium is a multi-valence element ($V^{+1} \dots V^{+5}$), the V-O phase diagram has many compound phases of V-O. Magneli phases with the general form V_nO_{2n-1} where n is an integer and $n \geq 2$. In order to synthesise VO_2 oxygen pressure must be monitored carefully [1]. (see **Table 1.3**). VO_2 exhibits a first order semiconductor-to-metal transition at about 68°C [2]. Below 68°C it has a high IR transmittance (see **Fig.1.1**) and is a semiconductor with a monoclinic structure belonging to phase group C2/m with lattice constants $a = 5.752 \text{ \AA}$, $b = 4.538 \text{ \AA}$, and $c = 5.383 \text{ \AA}$ whereas above this temperature it becomes metallic and is highly reflective with a tetragonal rutile structure, having space group P42/mnm with typical lattice constants $a = 4.530 \text{ \AA}$ and $c = 2.869 \text{ \AA}$ [3]. Table 1.1 lists the lattice constants of VO_2 in both phases.

TABLE 1.1: Summary of crystal structure, space group, and lattice constants of VO_2 in two phases [5].

Phase	Space Group	Lattice Constant ($\text{\AA}$)
Monoclinic distorted rutile structure	P21/c	$a = 5.752 \text{ \AA}$, $b = 4.538 \text{ \AA}$, and $c = 5.383 \text{ \AA}$
Tetragonal rutile structure	P42/mnm	$a = b = 4.530 \text{ \AA}$ and $c = 2.869 \text{ \AA}$

The insulator-to-metal transition temperature of 68°C in VO_2 can be lowered further to be at room temperature. This may be accomplished by doping it with high-valent transition metals such as tungsten, molybdenum, and niobium. Muraoka *et. al.* found Tungsten to be the most effective dopant, with an effect of $\sim -23\text{K/at. \% W}$ lowering of the temperature [3]. The thermochromic transition temperature of 68°C can be lowered to 25°C , and this is the ideal transition for nano- VO_2 and it can be used in design and fabrication of ‘smart windows’ for buildings so that efficient use can be made of the incident solar radiation.

V-O



V_nO_{2n-1}	$T_{tr}[K]$
V_2O_3	155
V_3O_5	430
V_4O_7	238
V_5O_9	135
V_6O_{11}	170
V_7O_{13}	---
V_8O_{15}	68
V_9O_{17}	79
VO_2	340

FIGURE 1.1: Phase diagram of Vanadium Oxides (V-O) with corresponding transition temperature [28].

Vanadium dioxide (VO_2) film is difficult to obtain since the V-O phase diagram has got many phases of V-O (see **Fig.1.1**), one has to make sure to use the correct amount of oxygen content.

TABLE 1.3: Selected data of vanadium oxides, ordered in terms of oxygen content. The second column shows the transition temperature for each oxide. The third column shows the melting temperatures of the selected materials [16]. VO_2 is the candidate chosen for study in this project, where T_r and T_m stands for transition and melting temperatures respectively.

Compound	T_t	Color	T_m
VO	-147°C	grey	
V_2O_3	-105°C	black	1970°C
V_5O_9	-138°C		
VO_2	+68°C [1 - 5, 8, 16]	dark blue	1976°C
V_6O_{13}	-123°C		700°C
V_2O_5	+375°C	yellow	685°C

1.2 Stresses in thin films

Stress is the mechanical property in the material which relates to deformation caused by an applied load or force and includes elastic modulus and strength. Stress is an endemic problem in vapour deposition films. The stress in thin films is revealed in different ways, either by the interface stress due to lattice matching, thermal expansion mismatching, and stress due to defect formation during film growth. These stresses can alter the service lifetime of coatings which experience additional external stresses (e.g. thermal or mechanical loading), and these can cause delamination and fracture of the film.

The delamination of the thin films is an effect that is very important in many areas of fundamental and applied research, as well as thin films itself. Stresses in the thin film deposited on rigid surface are usually caused by different thermal expansion coefficient of the substrate and the thin film material. If these stresses are compressive, they can lead to a delamination forming a web of blisters of different morphologies [8, 12, 16].

1.3 Solid State Interaction

A lot of work has been reported on thin film interactions between two different elements or compounds when in contact. Usually two thin films of these materials are brought into contact with one another by sequential evaporation of one film on top of the other on a non-reactive substrate. When these films are in contact and their temperature is raised sufficiently, a reaction between them may occur. Several methods have been developed to predict whether a reaction between VO_2 and thin metals will take place or not, and are discussed in this report. **Fig. 1.3** shows an example of Si and Cr reaction to form CrSi which best illustrates the mechanism [18]. This investigation looks at interfacial reactions between VO_2 and thin metal films. In this work we look at the thermodynamic stability of VO_2 in contact with thin metal films and develop rules based on the thermodynamics to predict whether a reaction between VO_2 and metals will take place or not.

1.3.1 Thermodynamics

The study of phase transformations is concerned with how phases in an alloy transform into a new phase or mixture of phases [26]. The thermodynamics in physical metallurgy allows one to predict whether a certain system is in equilibrium or not. These systems can either be metal-metal, metal silicides, metal oxides etc. In considering phase formation we are always concerned with changes towards equilibrium and therefore thermodynamics is a powerful tool. Although thermodynamics plays a major role in predicting phase formation it should be noted however that the rate at which equilibrium is reached cannot be determined by thermodynamics alone.

When two solid films are in contact, the transformation (formation of a new phase) may or may not occur and if phase transformation occurs it does so in order to lower the energy of a system. If the initial stage is unstable, a transformation to a new more stable state may occur [6]. This transformation will continue until the most stable state possible is reached and, no more

transformation may occur beyond this state i.e. no further chemical reaction may occur between the two films.

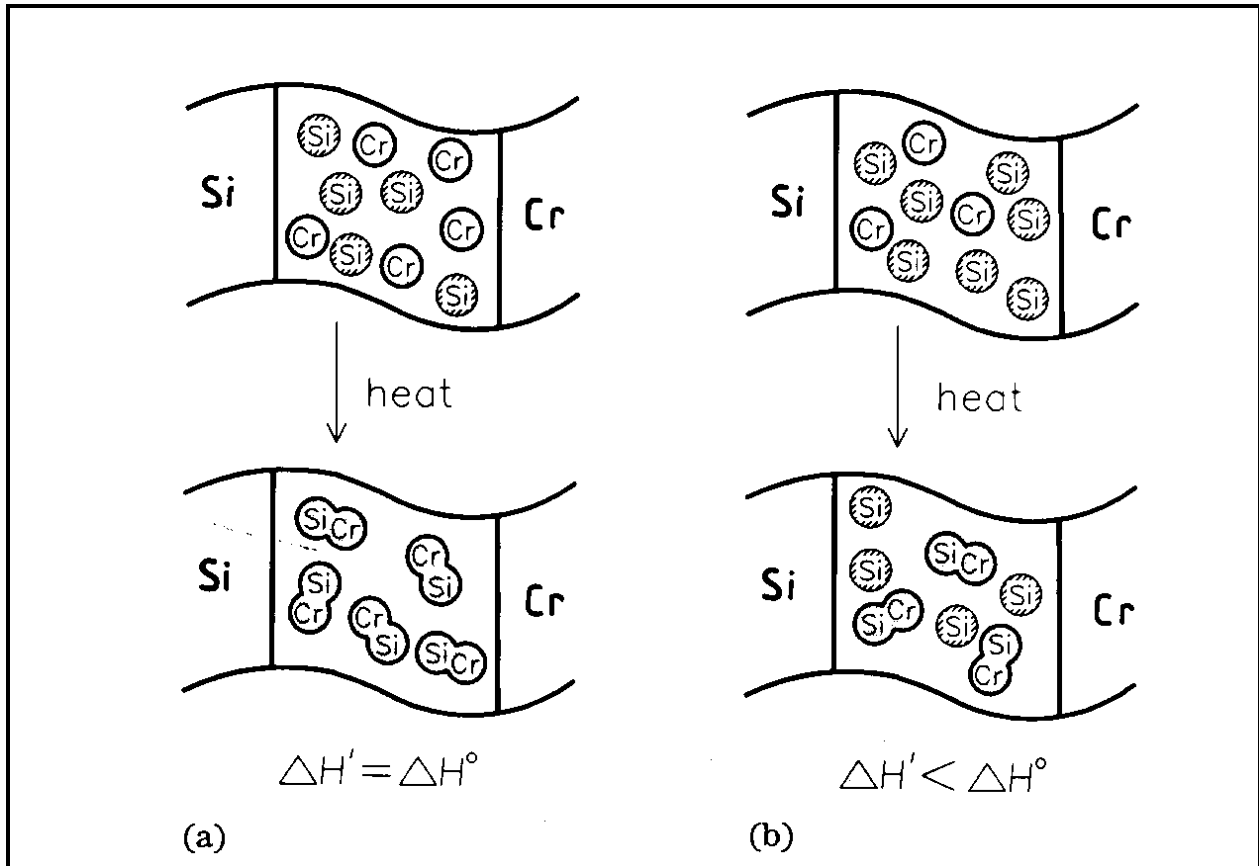


FIGURE 1.3: Schematic diagram of interaction between Cr and Si atoms to form CrSi. (a) There are five atoms of each element; five molecules of CrSi would be formed. (b) There are three atoms of Cr and seven atoms of Si; three molecules of CrSi would be formed with four Si atoms being in excess. Cr is the limiting element and EHF ($\Delta H'$) for this case would be less than the standard heat of formation (ΔH°) [18].

Clearly for one to be able to tell whether a certain phase transformation will or will not occur one will have to be able to measure the phase stability related to those particular phases. That is where thermodynamics is useful; it provides a way in which phase stability may be measured. For all transformations that occur at constant temperature and pressure, according to thermodynamics their relative stability may be determined by the system's Gibbs free energy (G).

The Gibbs free energy of a system is defined by

$$G = H - TS \quad (1.1)$$

Where H is the enthalpy, T the absolute temperature and S is the entropy of the system. Enthalpy is a measure of the heat content of a system and is given by

$$H = E + PV \quad (1.2)$$

Where E is the internal energy of the system, P is the pressure and V its volume. A system is said to be in equilibrium when it is in its most stable state possible. An important consequence of the laws of classical thermodynamics is that at constant temperature and pressure a closed system (i.e. one of fixed mass and composition) will be in stable equilibrium if it has the lowest possible value of the Gibbs free energy or in mathematical terms

$$dG = 0 \quad (1.3)$$

Fig.1.4 is a graphical illustration of the definition of equilibrium. If it were possible to evaluate the free energy of a given system for all possible configurations, the stable equilibrium configuration will be found to have the lowest Gibbs free energy. At this point slight changes in atomic configuration to a first approximation produce no change in G. However, there may be always another configuration in **Fig.1.4 [6]** which lies at a local minimum in Gibbs free energy and therefore also satisfies eq.1.3, but which does not have the lowest possible value of G. Such configurations are called metastable equilibrium states. Therefore a necessary criterion for a phase transformation is

$$\Delta G = G_2 - G_1 < 0 \quad (1.4)$$

where G_1 and G_2 are the Gibbs free energies of the initial and final states respectively. The transformation need not go directly to the stable equilibrium state but can pass through a whole series of intermediate metastable states.

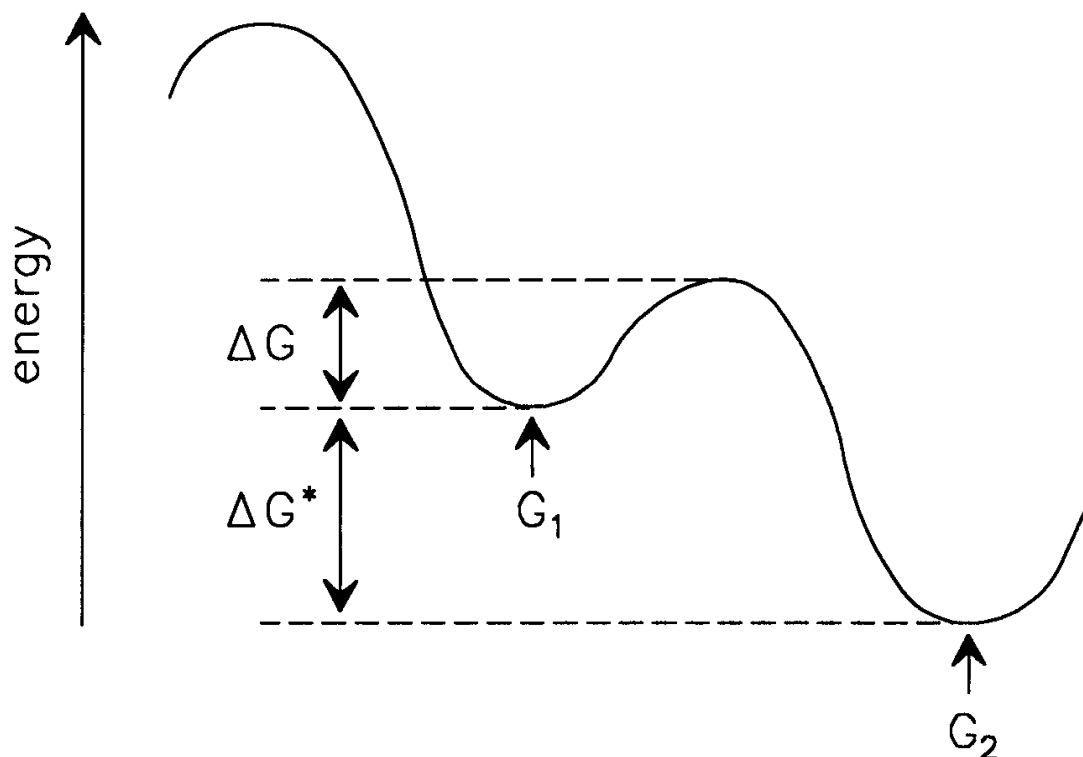


FIGURE 1.4 [6]: A hypothetical Gibbs function, showing metastable state G_1 and stable G_2 since it has the lowest free energy and is therefore arrangement when the system is at stable equilibrium. It also indicates a barrier that must be overcome by an atom that changes its Gibbs function value from G_1 to G_2 . ΔG^* is the overall change in the Gibbs function value.

Classical thermodynamics does not provide the answer as to how fast a transformation will take place. For the change in Gibbs free energy given by

$$\Delta G = \Delta H - T\Delta S \quad (1.5)$$

ΔH is a good measurement of the change in free energy ΔG , because ΔS is usually only of the order of 0.001 kJ/deg/mol for solid state reaction. Therefore term $T\Delta S$ is very small for solid state reactions. Therefore Gibbs free energy may be approximated:

$$\Delta G \approx \Delta H \quad (1.6)$$

The heat of reaction can be calculated if the enthalpy of the products and reactants are known. It is given by the difference between the enthalpy of the product at a certain temperature T and that

of the reactants at the same temperature. The standard enthalpy used in this case is the standard heat of formation at 298 K and at 1 atmosphere. If the heat of reaction is negative then it means that the reaction is thermodynamically possible. But this does not tell us what the resulting product will be. The model that can be used to predict the resulting product is called the Effective Heat of Formation (EHF) model.

1.3.2 The Miedema model

The Miedema model can be used to calculate the enthalpy of formation in binary liquid and solid phases. Using this model, the enthalpy of formation can be predicted for various atomic concentrations (see **Fig. 1.5**). The macroscopic atom model of Miedema for calculating heats of formation is a semi-empirical model alloy cohesion involving essentially only two material constants for each element [19, 20]. Although the model is semi-empirical, these constants are introduced by a consideration of the underlying physical ideas thought to play a role in the cohesion of alloys. On the assumption that properties of the bulk metal can be assigned to macroscopic “atoms” the heat of formation may be calculated as a function of concentration, where the electron density at the surface of the Wigner-Seitz cell, n_{ws} , and an adjusted value of the work function, ϕ^* , are the material constants. For non-transition metals the values of n_{ws} are easily available but for transition metals estimated values of n_{ws} are used. The assumption made during this estimation is that n_{ws} can be represented by

$$(n_{ws})^2 = \frac{k}{V} \quad (1.7)$$

where k is the experimental ratio of bulk modulus and V is the molar volume for pure metals.

The work function ϕ^* otherwise known as the Miedema electronegativity parameter is also very important parameter and is used to characterise metals using the Miedema model. For transition metals this parameter is given by

$$\phi^* = 5.2 \left(\frac{Z}{V} \right)^{\frac{1}{3}} + 0.2 \quad (1.8)$$

where Z is the number of valence electrons per atom.

For non transition metals ϕ^* is given by

$$\phi^* = 5.2 \left(\frac{Z}{V} \right)^{\frac{1}{3}} + 0.7 \quad (1.9)$$

where Z is the number of valence electrons per atom.

According to the Miedema model, the enthalpy of formation is given by

$$\Delta H^{formation} \propto \left[-P(\Delta\phi^*)^2 + Q \left(\Delta n_{WS}^{\frac{1}{3}} \right)^2 \right] \quad (1.10)$$

In the case of transition metals alloyed with polyvalent non-transition metals, a term R^* is introduced in eq.1.10. The heat of formation in this case is then given by

$$\Delta H^{formation} \propto \left[-P(\Delta\phi^*)^2 + Q \left(\Delta n_{WS}^{\frac{1}{3}} \right)^2 - R^* \right] \quad (1.11)$$

where P and Q are proportionality constants.

1.3.3 The Effective Heat of Formation

There has been considerable interest in predicting first phase compound formation and subsequent phase formation sequence in binary thin film systems [18]. It has been established experimentally that, unlike in the bulk case, not all of the compound phases present in the equilibrium phase diagram are observed [18]. In the case of silicides for instance, only one compound phase usually forms between the two components, silicon, and metal.

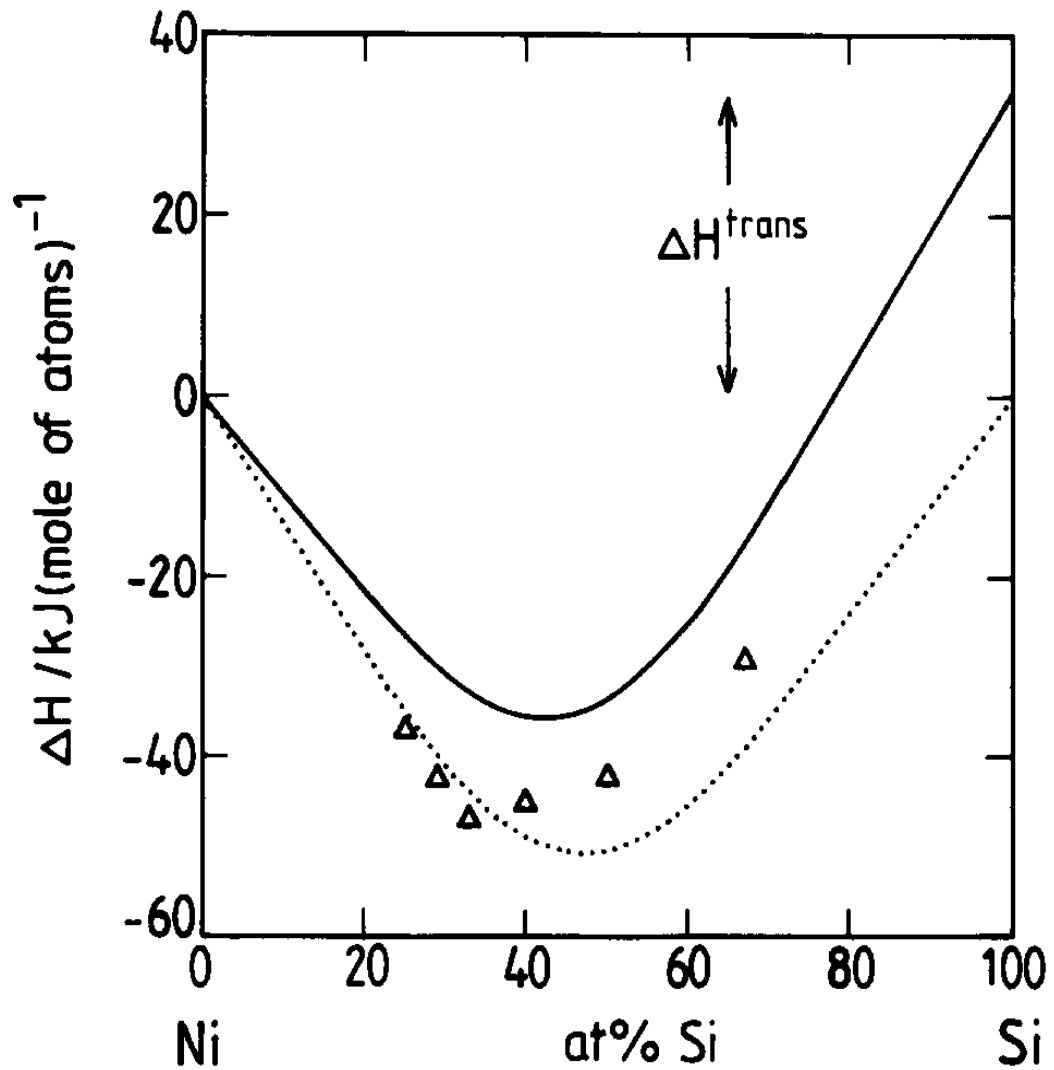


FIGURE 1.5: The dotted line gives the value of the heats of formation for the Ni-Si system calculated according to the semi empirical model of Miedema. By introducing a correction factor ΔH^{trans} whose value is 34 kJ/(mol.at) for silicon, the semi-conducting element is converted into a hypothetical metallic one and the values corresponding to the solid line are obtained, with the triangles indicating the experimental values of the heats of formation [18].

The effective heat of formation model can be used to predict first formation as well as formation sequence in binary thin film systems. This model makes direct use of thermodynamic data and enables the calculation of heat of formation as a function of atomic concentration of the reactants [17]. For two solid thin films in contact with one another, phase formation at an interface is non-equilibrium process. For such solid-state interactions it has been observed that only one compound phase forms at a particular interface.

The effective heat of formation ($\Delta H'$) is given by

$$\Delta H' = \Delta H^0 \left(\frac{\text{effective concentration of limiting element}}{\text{compound concentration of limiting element}} \right), \quad (1.12)$$

is used to predicting the phase formation sequence. Where values of ΔH^0 (standard heat of formation) are known, effective heats of formation can be calculated as the function of the concentration of the reacting species. **Fig. 1.6** shows a linear relationship between the effective heats of formation of various Ti-Si binary phases and the concentration of the reacting elements. Each triangle of the effective heat of formation diagram presents the energy released during the formation of a certain Ti-Si phase as a function of concentration.

Where $\Delta H'$ and ΔH^0 are measured in kJ per mole per atom and are known, effective heat of formation can be calculated as the function of the concentration of the reacting species. **Fig. 1.6** illustrates compound phases that are sequentially formed using EHF model in Ti – Si system. There are five equilibrium compound phases, namely Ti_3Si ; Ti_5Si_3 ; Ti_5Si_4 ; TiSi and TiSi_2 .

The possibility also exists that the true effective concentration could lie somewhere between the two eutectics. The effect of eutectic concentrations which are close to each other in temperature on the effective concentration at the growth interface is not yet well understood and needs further study [10]. In **table 1.4** the effective heats of formation for Ti-Si are calculated, assuming the effective concentration to be either at the concentration of the Si-rich or the Ti-rich eutectic. It is immediately apparent that an effective concentration of 84 at. % Si favours the formation of the silicon-rich silicide TiSi_2 , with $\Delta H' = -27.4 \text{ kJ (mol at.)}^{-1}$ (see **Fig. 1.6**), while an effective concentration of 14 at. % Si favours the more titanium-rich silicide Ti_3Si .

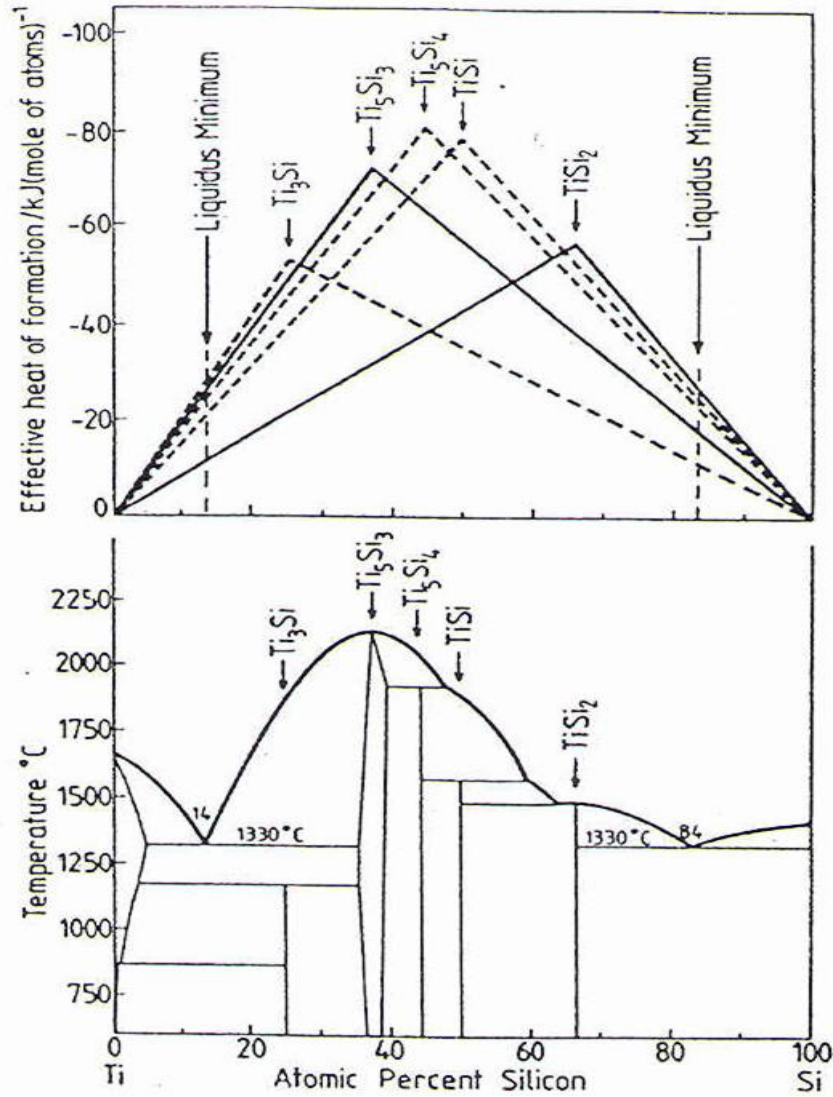


FIGURE 1.6: The above diagram shows the phase diagram and effective heat formation (EHF) of Ti-Si binary system. Each shape of triangle in EHF above the phase diagram represents the amount of energy per mole of atoms that is consumed in the phase formation composition, the dashed triangles show non-congruently melting phases [18].

The true effective concentration could therefore possibly be anywhere between these two values and the EHF model therefore predicts a whole range of phases.

Using equation 1.12 calculate the Effective heat of formation for Ti_3Si . We assume that the effective concentration of Ti at the growth interface is 50% and Si is 50%,

Therefore we find:

$$\text{Heat of formation } \Delta H^\circ = -53 \text{ kJ/mol/at}$$

$$\text{Compound to be formed} = \text{Ti}_{0.750}\text{Si}_{0.25} (\text{Ti}_3\text{Si})$$

$$\text{Effective concentration} = \text{Ti}_{0.160}\text{Si}_{0.840}$$

The limiting element is Ti. Therefore applying equation 1.12 leads to

$$\Delta H' = \Delta H^\circ (0.160/0.750) = -11.3 \text{ kJ/mol/atom.}$$

Equation 1.12, which defines the effective heat of formation, can be derived as follows.

Consider the formation of the compound A_xB_y (see **Fig.1.7**) at the interface between A and B to be given by the equation

$$z(X_a + Y_b) \rightarrow z(A_xB_y) \quad (1.13)$$

Let N be the total number of atoms available for reaction in the reaction zone where

$N = N_A + N_B$ with N_A being the number of atoms of A and N_B is the total number of atoms of B.

Let M be the total number of atoms consumed in formation of A_xB_y i.e.

$$M = zx + zy = M_A + M_B \quad (1.14)$$

The effective concentration of atom A is

$$C_e^A = \frac{N_A}{N} \quad (1.15)$$

The effective (available) concentration of atom B is

$$C_e^B = \frac{N_B}{N} \quad (1.16)$$

The compound concentration of B in A_xB_y is

$$C_c^A = \frac{x}{x+y} \quad (1.17)$$

If A is the limiting number of atoms during the formation of A_xB_y , its atoms are fully consumed, whilst the atoms of B will be in excess. It follows that

$$M_A = N_A = NC_e^A \quad (1.18)$$

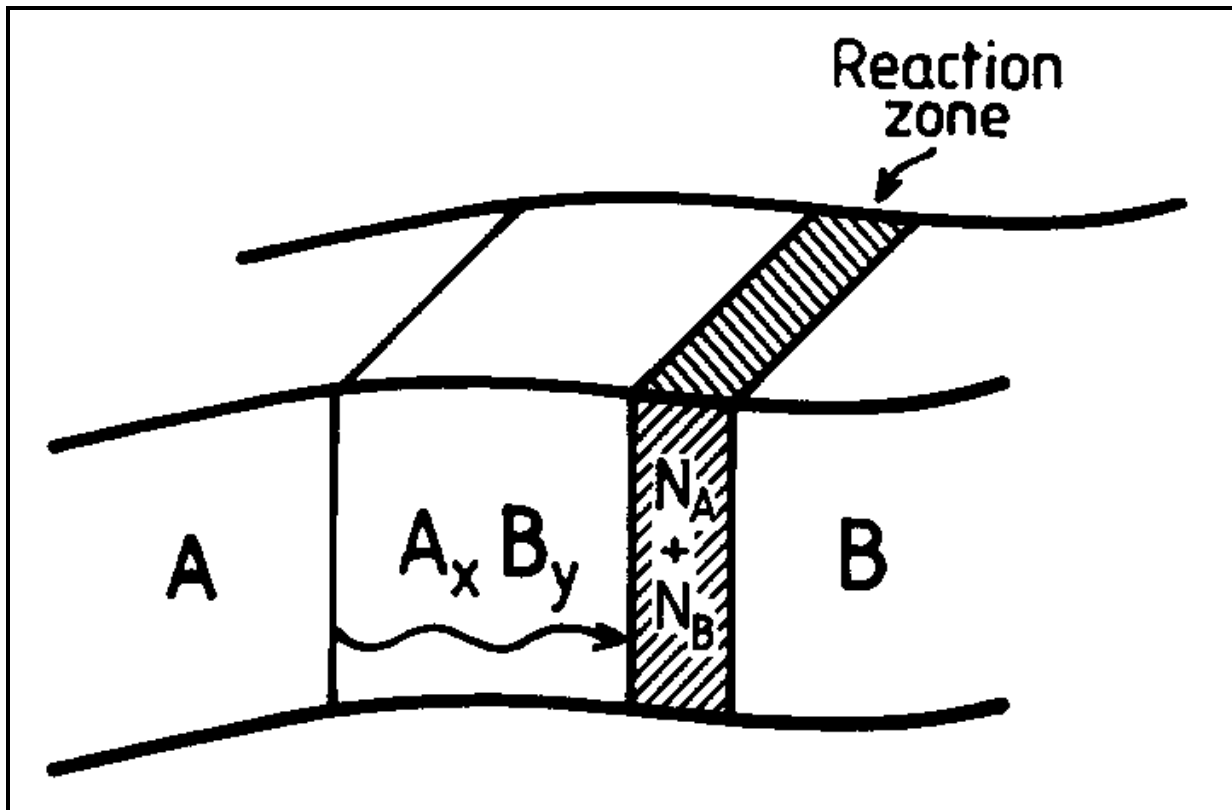


FIGURE 1.7: Schematic diagram of the formation of a compound A_xB_y at the reaction zone [18].

During the formation of A_xB_y , atoms are consumed in the ratio

$$\frac{x}{y} = \frac{M_A}{M_B} \quad (1.19)$$

From eq.1.14 and 1.19 we have

$$\begin{aligned} M &= M_A \left[1 + \frac{y}{x} \right] \\ M &= \frac{M_A}{C_e^A} \end{aligned} \quad (1.20)$$

From eq.1.18 and eq.1.20 we have

$$\frac{M}{N} = \frac{C_e^A}{C_c^A} \quad (1.21)$$

The heat of formation ΔH° when expressed in J/mol/atom is the heat released when a mole or Avocado's number (Av) of atoms is consumed during the formation of A_xB_y .

The consumption of M atoms releases $\frac{M}{(Av)} \Delta H^\circ$ of heat of formation. The number of moles of available atoms is $\frac{N}{(Av)}$. Therefore the heat released per mole of available atoms is

$$\Delta H^\circ \left(\frac{\frac{M}{(Av)}}{\frac{N}{(Av)}} \right) = \Delta H^\circ \frac{M}{N} \quad (1.22)$$

For non-equilibrium reaction such as that described above, the effective heat of formation can be defined as

$$\Delta H' = \Delta H^\circ \left(\frac{C_e^A}{C_c^A} \right) \quad (1.23)$$

Or

$$\Delta H' = \Delta H^\circ \left(\frac{\text{effective concentration of limiting element}}{\text{compound concentration of limiting element}} \right) \quad (1.24)$$

The success of the effective heat of formation (EHF) model for predicting phase formation is due to the fact that heats of formation, as well as concentration, are taken into account.

Table 1.4

Effective heats of formation ($\Delta H'$) for the titanium silicides, calculated at the concentrations of the two lowest eutectics (both at 1330°C) at 14 and 84 at.% silicon in the Ti-Si phase diagram. The predicted phases are those with the most negative $\Delta H'$ and are shown as bold numbers [18].

Phase	Compound Concentration	ΔH° (kJ (mol at.) ⁻¹)	Effective concentration			
			Ti_{0.160}Si_{0.840}		Ti_{0.860}Si_{0.140}	
			Limiting element	$\Delta H'$ (kJ (mol at.) ⁻¹)	Limiting element	$\Delta H'$ (kJ (mol at.) ⁻¹)
Ti ₃ Si	Ti _{0.750} Si _{0.250}	-53	Ti	-11.3	Si	-29.7
Ti ₅ Si ₃	Ti _{0.625} Si _{0.375}	-72	Ti	-18.4	Si	-26.9
Ti ₅ Si ₄	Ti _{0.556} Si _{0.444}	-81	Ti	-23.3	Si	-25.5
TiSi	Ti _{0.500} Si _{0.500}	-79	Ti	-25.3	Si	-22.1
TiSi ₄	Ti _{0.333} Si _{0.667}	-57	Ti	-27.4	Si	-12.0

1.4 Prediction of Interaction

There is a model of predicting whether a metal will react with SiO₂ or not [21]. This model uses both electronegativities and heats of reaction. The reaction between a metal and oxide may be written as:

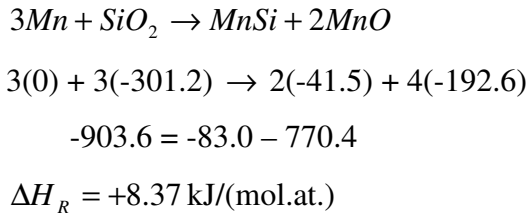


where M is the metal and it is assumed that the resulting products are a metal silicide and a metal oxide. The reactions considered are those that happen at constant temperature and pressure, where the change in Gibbs energy is given by

$$\Delta G = \Delta H - T\Delta S \quad (1.26)$$

With ΔH is the change in enthalpy (or heat of reaction). $\Delta S \approx 0$, since it is assumed that both reactants and products are solids. ΔG is therefore approximated by the enthalpy. If the enthalpy is less than zero, then the reaction between SiO_2 and metal is thermodynamically possible.

Take for an example a reaction between SiO_2 and Mn to form MnSi and MnO. The heat of reaction in this case is calculated as follows:



Working out the other possibilities for this system it is found that all ΔH_R are positive.

These tell us that Mn does not react with SiO_2 .

Pretorius et al [21] have also used electronegativity to predict whether a reaction between a metal and SiO_2 is possible. A plot of calculated standard heats of reaction ΔH_R for some metals was plotted as a function of the average of three electronegativities (average of relative compactness, Pauling, and Allred-Rochow electronegativities), see **Fig.1.9**. A linear relationship between the electronegativities of the metals and their calculated standard heats of formation was obtained.

It was found that metals with electronegativities of greater than about 1.5 on the Pauling scale do not react with SiO_2 whereas those with electronegativities of less than about 1.5 do react with SiO_2 .

1.4.1 Prediction of reaction using ternary phase diagrams.

Ternary phase diagrams may be used to predict the stability of a compound involving three or less elements each in contact with one element of the compound. Beyers used W-Si-O, Ti-Si-O,

Ti-Si-N, and Ti-Al-N systems as examples to demonstrate the use of ternary phase diagrams to explain the stability of refractory metals, silicides, and nitrides during various integrated circuit processing steps [22, 23].

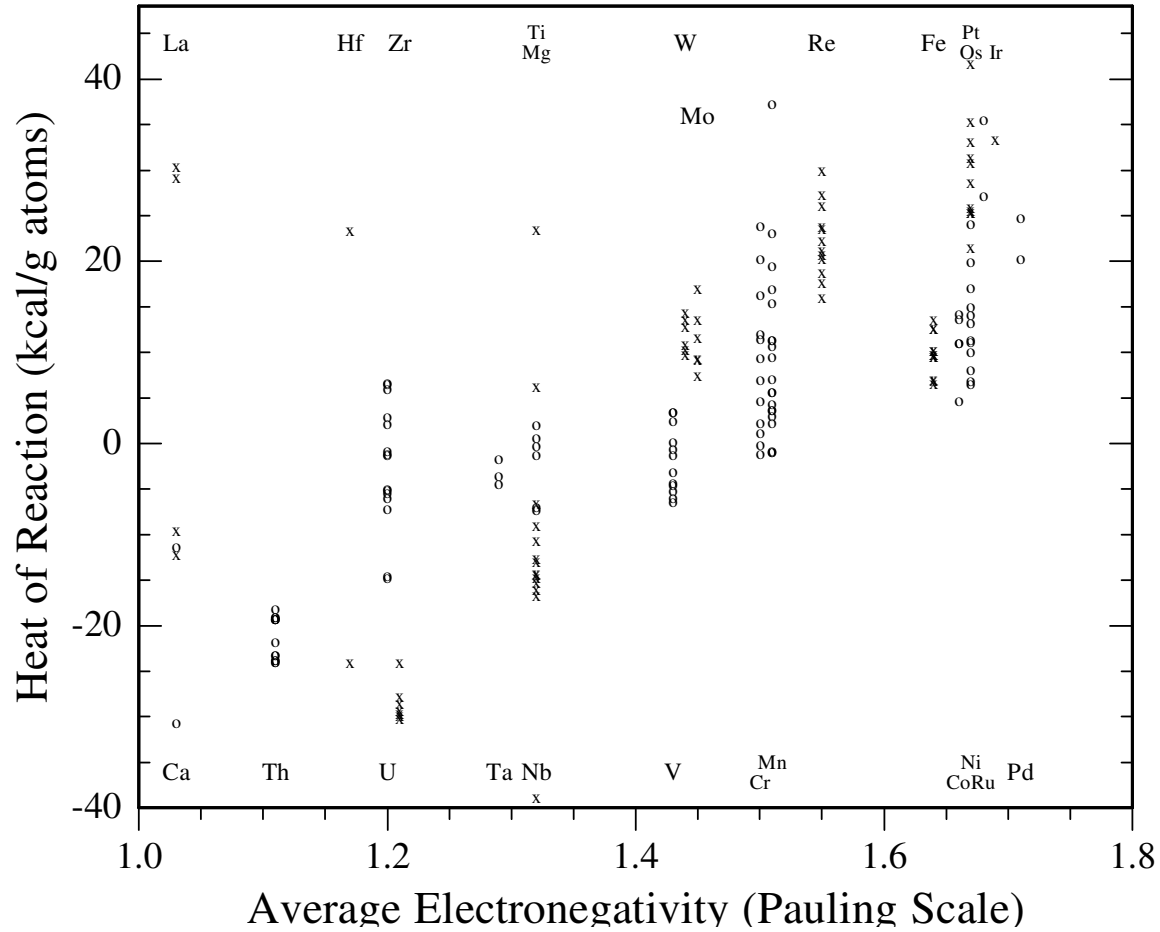


FIGURE 1.8: [21] Heats of reaction for all possible combinations of various metals in interaction with SiO_2 . The plot shows heats of reaction plotted on the vertical axis and electronegativities on horizontal axis. The crosses appearing refer to elements at the top and open circles to elements at the bottom.

According to the Gibbs phase rule there can only be three phases in equilibrium in any portion of the phase diagram at fixed temperature and pressure. Regions of three-phase equilibrium form triangles in isothermal sections of the ternary phase diagram. The phases found at the corners of such triangles are thermodynamically stable when in contact with each other. The two-phase tie lines that are established by calculating the Gibbs free energy of reaction (heat of reaction in our case since) at the point where two possible tie lines would cross are used to determine regions of three-phase equilibrium. Crossing tie lines are forbidden because at the point of their intersection there would be a simultaneous coexistence of four phases, thus resulting in the violation of the Gibbs phase rule. The Gibbs phase rule states that *there is a maximum number of three phases in mutual equilibrium for an arbitrary composition*.

For example, one may want to know whether TiSi_2 is stable when in contact with SiO_2 at 700°C i.e. is there a tie line between TiSi_2 and SiO_2 at this temperature? The solution to this problem is obtained by considering all possible reactions between Ti oxide-Si couples and the TiSi_2 - SiO_2 couple (see **Table 1.5** and **Fig. 1.9**) [24]. Since the free energy change is negative in all cases, then a stable tie line exists between TiSi_2 and SiO_2 at this temperature. Therefore TiSi_2 is stable when in contact with SiO_2 at 700°C . The remaining stable tie lines in the Ti-Si-O phase diagram are evaluated in a similar way.

TABLE 1.5: Free energy calculation showing that a stable tie line exist between TiSi_2 and SiO_2 at 700°C [24].

Tie line reactions	ΔG , kJ/mole.at
$2 \text{ TiO} + 5 \text{ Si} = 2 \text{ TiSi}_2 + 1 \text{ SiO}_2$	-17.82
$2 \text{ Ti}_2\text{O}_3 + 11 \text{ Si} = 4 \text{ TiSi}_2 + 3 \text{ SiO}_2$	-16.80
$2 \text{ Ti}_3\text{O}_5 + 17 \text{ Si} = 6 \text{ TiSi}_2 + 5 \text{ SiO}_2$	-18.96
$1 \text{ TiO}_2 + 3 \text{ Si} = 1 \text{ TiSi}_2 + 1 \text{ SiO}_2$	-21.65

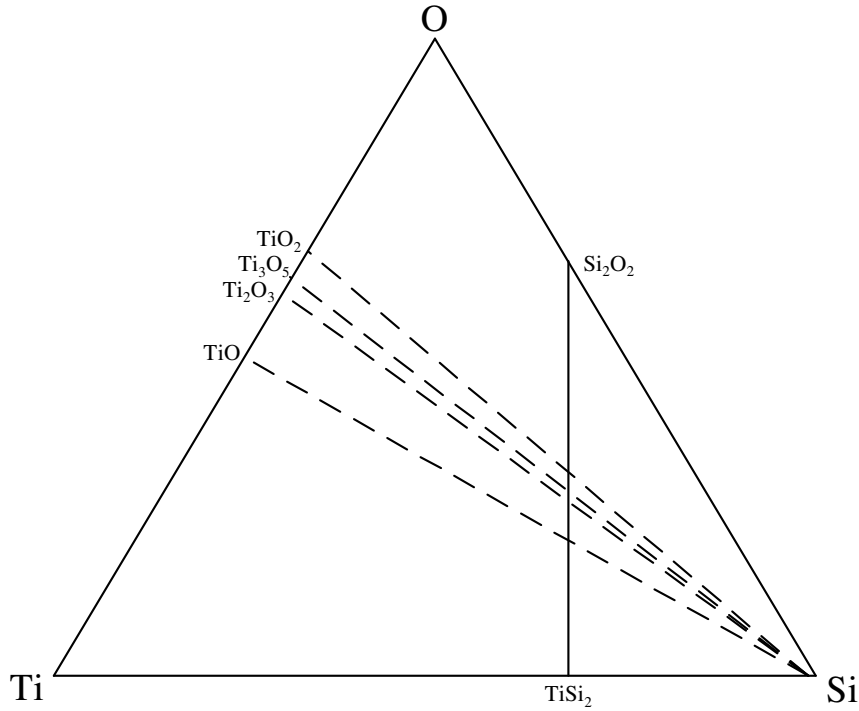


FIGURE 1.9: The ternary phase diagram for Ti-Si-O. Solid line (or tie line) indicates stability while broken lines (unstable), extracted from Table 1.5 chemical reactions [24].

1.5 Scope of this investigation

VO_2 has a great potential for the application as smart window coating. Vanadium dioxide (VO_2) exhibits a reversible MST at 68°C [1-7]. Below this transition temperature, it is a narrow band gap (0.65 eV) semiconductor with a monoclinic structure. Above 68°C , it transforms into a tetragonal (TiO_2) structure and exhibit metallic properties. This transition is accompanied by the abrupt change in the electrical resistivity, optical transmittance and reflectance. For example, the VO_2 film in the infrared region has a very low transmittance in the metallic phase and high transmittance in the semiconducting phase. This has lead to many applications of the material in infrared light especially as intelligent energy conserving window coating (smart window) [7, 30]. This material (VO_2) if in contact with various metals and its temperature is raised new stable phases maybe formed which can be used in various applications. Understanding the thermodynamics of the stability of VO_2 when in contact with metals gives a better understanding

of the future possibilities in the applications of these newly formed phases from VO₂-metal, interactions. As VO₂ film remained a challenge to synthesis because of the phase diagram which has many V-O phases present, a correct control of oxygen is critical during deposition. The study concern itself with interaction between VO₂ and thin metal films. The sample characterization methods used to determine the layer thicknesses of the deposited materials and after annealing are Rutherford Backscattering Spectroscopy (RBS) and X-Ray Diffraction. These sample characterizations are described in **chapter 2** in more details. The film synthesis and characterization are described in **chapter 3**. **Chapter 4** looks at the interaction between VO₂ and these (Pt, Co, Ni, Pd, Hf, and Al) thin metal films. The experimental results are then compared with theoretically predicted heats of reaction from the literature and correlations with the average electronegativity of the metals are discussed in **Chapter 5**. The ternary phase diagrams could also be used to explain the experimental results [24]. **Chapter 6** gives a summary and the conclusion of this study.

CHAPTER 2

SAMPLE PREPARATION AND CHARACTERISATION TECHNIQUES.

In this study, radio frequency reactive sputtering and electron-beam evaporation system were used to deposit VO₂ and thin metal films onto glass substrates. The films were sequentially deposited on top of each other and were characterized using several techniques i.e. X-ray diffraction, Atomic Force Microscopy, UV-VIS spectrometer, and Rutherford Backscattering spectrometry. X-ray diffraction was employed for phase identification. The surfaces of the films were characterised by atomic resolution by atomic force microscopy and Rutherford backscattering spectrometry. Samples were also optically examined using a UV – VIS spectrometer.

In this chapter, the operation associated with these techniques is briefly described.

2.1 Sample Preparation

2.1.1 Substrate preparation and cleaning

Square corning glasses of 1cm edge were chemically cleaned following a simple sequence. The following procedure was used. Samples were firstly dipped in methanol, followed by acetone, then trichloroethylene, then acetone, and finally methanol. Then the samples were rinsed in ionised water. The stirring was done using an ultrasound bath. The samples were then attached onto aluminium holders, and these holders were then placed onto a rotatable sample holder which was then put inside a high vacuum system (see Fig. 2.2).

2.1.2 Radio frequency reactive sputtering

Sputtering provides a very useful method for preparing a wide range of thin films with good control over film properties. It is widely used in industry from microelectronics to decorative coating of automobiles.

Radio frequency reactive sputtering: When a solid target is bombarded with energetic particles such as accelerated ions, surface atoms of the solids are partly scattered backward due to collisions between the surface atoms and the energetic particles. This phenomenon is known as sputtering and is often used to deposit thin films.

The sputter deposition system is composed of a pair of planar electrodes, (see **Fig. 2.1**). One of the electrodes is a cold cathode and the other is anode. A target material that will be used in this work is vanadium. The sputter chamber will be filled with the sputter gas, typically Argon.

The glow discharge is maintained under the application of the voltage between the electrodes. The Ar^+ ions generated in the glow discharge will be accelerated towards the cathode (vanadium). The bombardment of the target by these energetic positive ions causes the surface removal of target (vanadium) atoms. These Vanadium atoms will react with a partially filled oxygen gas in chamber besides Ar, the reactive gas will react with vanadium atoms forming a compound layer of VO_2 on the substrate which will be glass, only if oxygen gas is well controlled. This method is known as reactive sputtering [7]. This technique in this work has been used to deposit VO_2 on glass substrate forming VO_2/glass , after which a metal will be deposited on VO_2/glass using electron-beam deposition technique which is discuss next to form metal/ VO_2/glass .

2.1.3 Vacuum deposition

The evaporator has three crucibles into which elements to be evaporated are loaded. The crucibles can be moved from the outside so that each of the three crucibles can be placed in the path of the electron beam in turn. The electron beam supplies the heating to the crucibles. Crucibles were cleaned before introducing the elements to be evaporated. Each crucible is

separated and shielded from one adjacent to it by partition which is 20 mm in height to prevent cross-contamination during depositions. Electrons are supplied by the electron gun. The filament current can be varied thus changing the electron beam current which in turn alters the rate of deposition. Sample holders, each of which can take up to seven samples, are loaded face down on a rotating platform which can take up to six sample holders.

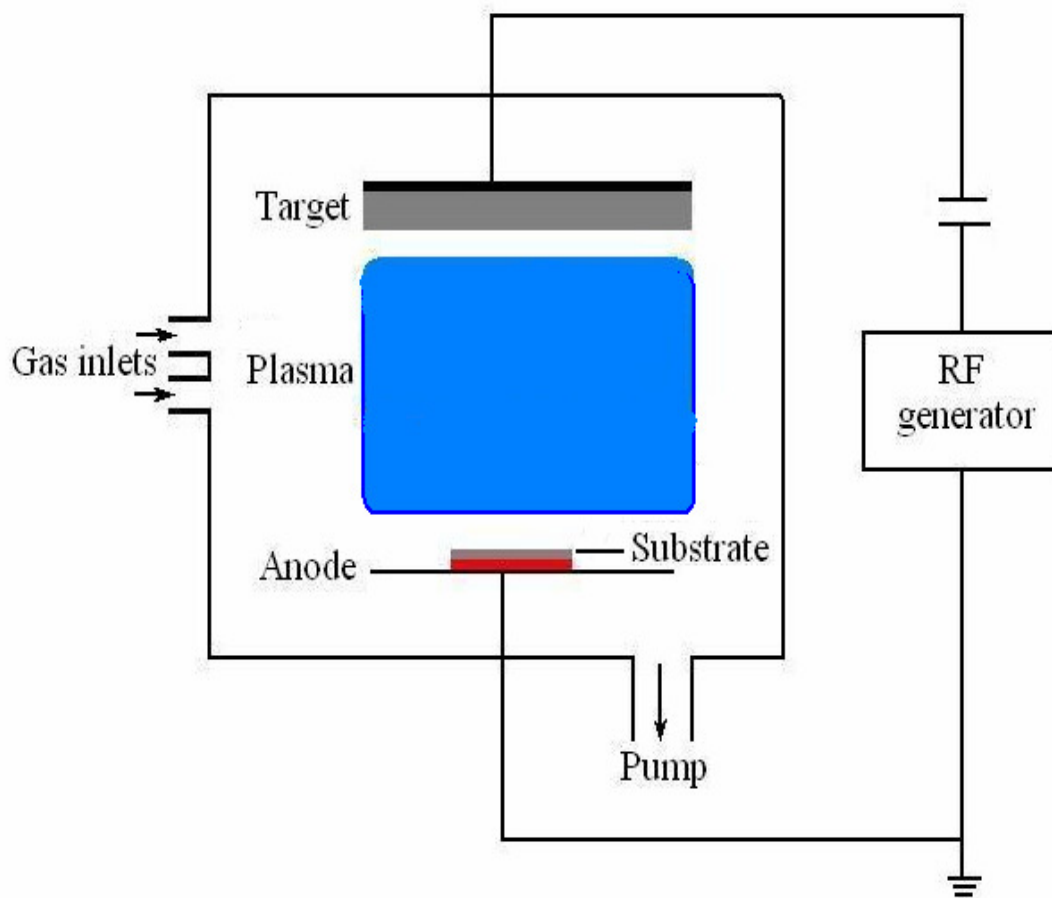


FIGURE 2.1: *RF reactive sputter deposition system [7].*

A quark monitor was used to find the rate at which depositions were done as well as thickness of evaporated layers. All depositions were done in vacuum. Vacuum was maintained by means of ion pumps, sublimation pumps, cryopanel and a turbo- pump. The top part of the evaporator can be isolated from the bottom part by means of a baffle valve (see **Fig.2.2**). This valve was kept closed during cleaning of crucibles and re-loading of samples, so that the bottom part was at a pressure of better than $\approx 10^{-8}$ kPa. Pressure measurements were taken by means of a penning gauge in the range

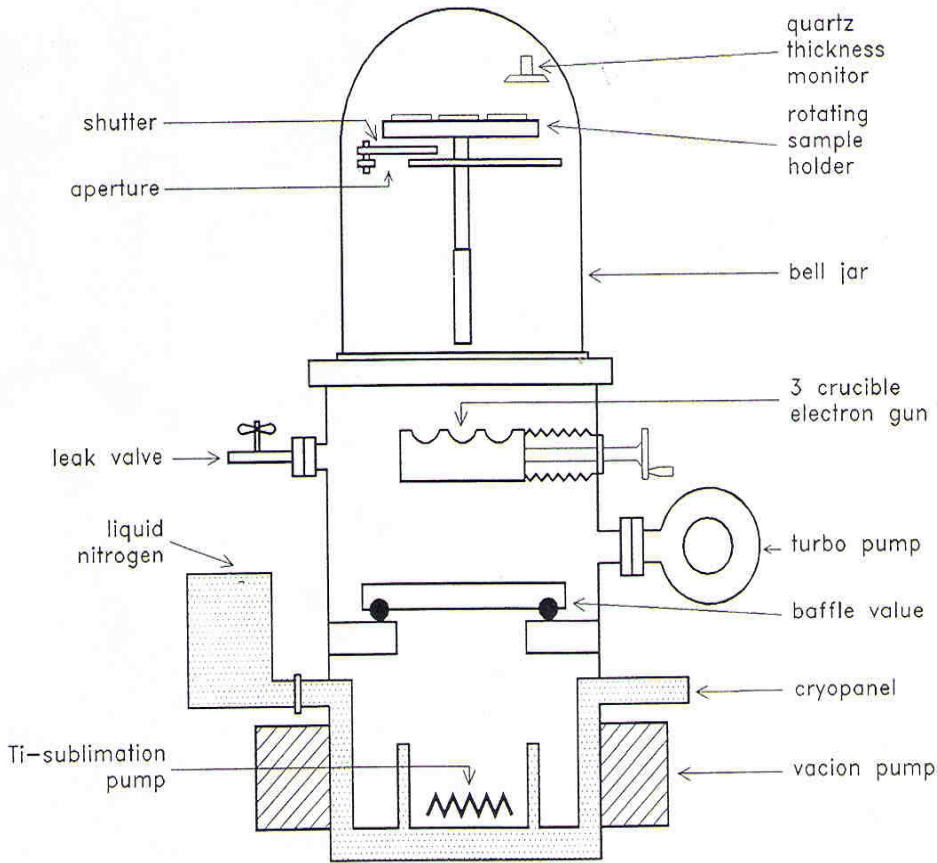


FIGURE 2.2: A schematic representation of the instrumental e-beam set up [13].

10^{-3} kPa to 10^{-8} kPa. The ion pump consists of pumping elements which are surrounded by a strong magnetic field. Each pumping elements consists of a multi-cell anode structure between two titanium cathode plates. A voltage of about 6000V is maintained between the anode and cathode. Electrons moving from cathode to anode are forced by the magnetic field to spiral, thus increasing their path and probability of colliding with gas molecules. Collisions ionise the gas.

Positively charged gas ions are accelerated by the electric field and move towards the titanium cathode. This effect sputters the titanium atoms. Titanium then getters the oxygen and nitrogen part of the gas.

The gettering action of the ion pumps is increased by sublimation and cryopumping. The turbo pump on the top part of the evaporator can reduce the pressure to about 10^{-5} kPa if left to pump overnight. On opening the baffle valve and pouring liquid nitrogen vacuum is improved to about 10^{-9} kPa. Vapours such as H_2O and CO_2 are trapped on the cooled surface of the cryopanel. Non-condensable gases are then carried down by the condensable vapour and then trapped within the condensate. Sublimation pumps are also used to further decrease the pressure to even better vacuum.

After evaporation samples were allowed to cool in vacuum for about two hours to prevent oxidation of the samples. As a further precaution vacuum was broken by means of dry high grade nitrogen. In this investigation, this technique was used to deposit metals on VO_2 /glass to form metal/ VO_2 /glass.

2.1.4 Vacuum annealing

After vacuum deposition was completed, the thin metal films were annealed to speed up the interaction between the metal film and the VO_2 film. All samples annealed were for time of 2 hours for each temperature and were left it to cool down slowly to room temperature, which took up to five hours to avoid any possible oxidation. Some samples were left unannealed as a reference to the annealed ones. The vacuum furnace was fitted with 6 boat carousel. Each boat could carry four samples. The furnace was fitted with a mechanical fore pump and a turbo-molecular pump. A cold trap filled with nitrogen also helped to reduce the pressure. All annealing were done at pressures below 10^{-7} kPa. The temperature was controlled by a microprocessor.

2.2 Characterization techniques

Various methods were used to identify compound phases that grew during heat treatment and sample thicknesses were also determined.

2.2.1 X-Ray diffraction

X-ray diffraction (XRD) is a powerful non-destructive technique for characterization of crystalline materials. It provides the information on structure, phase, preferred crystal orientation (texture) and other structural parameters, such as average grain size, crystallinity, strain and crystal defects [11].

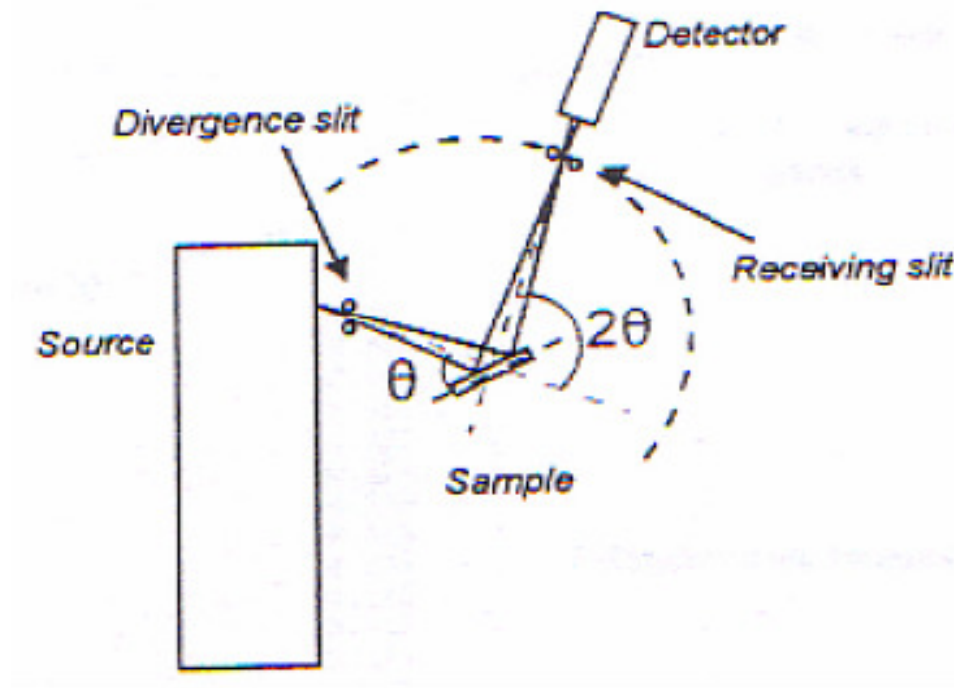


FIGURE 2.3:[14] XRD scanning principle, with detector moving along the diffractometer circle.

When a monochromatic X-ray beam with wavelength λ , the order of lattice spacing d , is projected onto a crystalline material at an angle θ , X-ray diffraction peaks are produced by constructive interference of monochromatic beam scattered from each set of lattice planes at specific angles. Constructive interference gives the diffraction peaks according to Bragg's law,

$$2d \sin \theta = n\lambda \quad (2.1)$$

where d is interplanar spacing, n is the order of the reflection, λ is the wavelength, and θ incident angle.

By varying the angle θ , the Bragg's Law condition is satisfied by different d - spacings in crystalline materials. Plotting the angular positions vs intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the material.

Fig. 2.3 Show the x-ray diffraction setup.

2.2.2 Rutherford Backscattering Spectrometry (RBS)

RBS is a very simple and fast method of obtaining elemental depth profiles in solids. It is very well suited for the study of thin films. The sample is bombarded by light ions having energies, usually in the range 1-3 MeV which are scattered on the solid to be investigated. At these low energies only elastic collisions occur, and this way nuclear reactions are avoided. An ion beam of positive charged particles (H^+ , He^+ or He^{++}) is directed to the sample, and then a solid detector is used to analyse the backscattered particles. Samples are placed in vacuum ($\approx 10^{-6}$ kPa) while being analysed. The sample normal is tilted 10 degrees with respect to the ion beam, and only those particles backscattered at 165 degrees are analysed by the detector. A permanent horseshoe magnet is used to prevent secondary electrons from escaping from the target.

In the first approximation we can describe Rutherford backscattering as an elastic hard-sphere collision between a high kinetic energy particle from the incident beam and a stationary particle located in the sample. Assuming conservation of momentum and kinetic energy, we can write the energy E_1 of the scattered projectile as

$$E_1 = E_0 \left(\frac{m_1 \cos \theta_1 \pm \sqrt{m_2^2 - m_1^2 (\sin \theta_1)^2}}{m_1 + m_2} \right)^2 \quad (2.2)$$

where particle 1 is the projectile with initial energy E_0 , particle 2 is the target nucleus, and θ_1 and θ_2 describe the backscattered angles of the particles relative to the incident trajectory (see **Fig.2.4**). The plus sign is taken when the mass of the projectile is less than that of the target, otherwise the minus sign is taken. While this equation correctly determines the backscattered energies relative to measurement angle, it does not describe the angular distribution of the backscattering probability. For this we need the differential cross-section of the backscattering:

$$\frac{d\omega}{d\Omega} = \left(\frac{z_1 z_2 e^2}{4E_0} \right)^2 \frac{1}{\left(\sin \frac{\theta_1}{2} \right)^4} \quad (2.3)$$

where Z_1 and Z_2 are the atomic numbers of the incident and target nuclei. These two equations together determine the probability and energy of a measurement over a differential solid angle at incident angle θ_1 for a single collision.

While large-angle scattering only occurs for ions which scatter off target nuclei, inelastic small angle scattering can also occur off the sample electrons. This results in a gradual decrease in ions which penetrate more deeply into the sample, so that backscattering off interior nuclei occurs with a lower “effective” incident energy. The amount by which the ion energy is lowered after passing through a given distance is referred to as the stopping power of the material and is dependent on the electron distribution. This energy loss varies continuously with respect to distance traversed, so that stopping power is expressed as

$$S(E) = -\frac{dE}{dx} \quad (2.4)$$

For high energy ions stopping power is usually proportional to $\frac{z_2}{E}$; however, precise calculation of stopping power is difficult to carry out with any accuracy. Stopping power has been tabulated for most material, and is generally given in units of eV (atom cm⁻²)⁻¹.

2.2.2.1 Instrumentation

An RBS instrument generally includes three essential components:

- An ion source, usually alpha particles (He⁺ ions) or, less commonly protons.
- A linear particle accelerator capable of accelerating incident ions to high energies, usually in the range 1-3 MeV.
- A detector capable of measuring the energies of backscattered ions over some range of angles.

Two common source/acceleration arrangements are used in commercial RBS system, working in either one or two stages.

One-stage consist of a He^+ source connected to an acceleration tube with a high positive potential applied to the ion source, and the ground at the end of the acceleration tube. This arrangement is simple and convenient, but it can be difficult to achieve energies of much more than 1 MeV due to the difficulty of applying a very high voltage to the system.

Two-stage system, or “tandem accelerator”, start with a source of He^- ions and position the positive terminal at the center of the acceleration tube. A stripper element included in the positive terminal removes electrons from ions which pass through, converting He^- ions to He^{++} ions. The ions thus start out being attracted to the terminal, pass through and become positive, and are repelled until they exit the tube at ground. This arrangement, though more complex, has the advantage of achieving higher accelerations with lower applied voltages: a typical tandem accelerator with an applied voltage of 750 kV can achieve ion energies of over 2 MeV.

Detector to measure backscattered energy are usually silicon surface barrier detector, a very thin layer (100 nm) of p-type silicon on an n-type substrate forming a p-n junction. Ions which reach the detector lose some of their energy to inelastic scattering from electrons, and some of these electrons gain enough energy to overcome the band gap between the semiconductor valence and conduction bands.

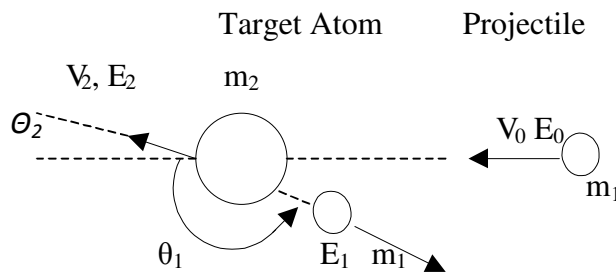


FIGURE 2.4: The geometry representation of elastic scattering of a projectile atom, mass m_1 , from a target atom, mass m_2 happened during the experiment in Rutherford Backscattering Spectrometry. This means that each ion incident on the detector will produce some number of electron-hole pairs which is dependent on the energy of the ion. These pairs can be detected by applying a voltage across the detector and measuring the current, providing an effective measurement of the ion energy.

2.2.3 UV-VIS-NIR Spectrometry for Optical measurements

Sunlight is seen to be white light or as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. Different molecules absorb radiation of different wavelengths, but many molecules absorb ultraviolet or visible light. The absorbance of solution is directly proportional to the attenuation of the beam, meaning if absorbance increases then attenuation of the beam also increases.

The optical transmission spectrophotometry are conducted from room temperature to high temperatures on a Cecil 2000 unit in the spectral range of 200-1100 nm [29]. It uses two different non cooled detectors. The film absorb at the range of 200 nm to 400 nm wavelength. It has heating device which heats up to 110 °C while taking measurements.

2.2.4 Atomic Force Microscopy (AFM)

The Atomic Force Microscope (AFM) is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries. The materials being investigated include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing [12]. By using AFM one can not only image the surface in atomic resolution but also measure the force at nano-newton scale. The publications related to the AFM are growing speedily since its birth.

The principles on how the AFM works are very simple. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si_3N_4 or Si, and extended down from the end of a cantilever.

The nanoscope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever (see **Fig.2.5**). As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode. The photo detector measures the difference in light intensities between the upper and lower photo detectors, and then converts to voltage. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode the piezo-electric transducer monitors real time height deviation. In the constant height mode the deflection force on the sample is recorded.

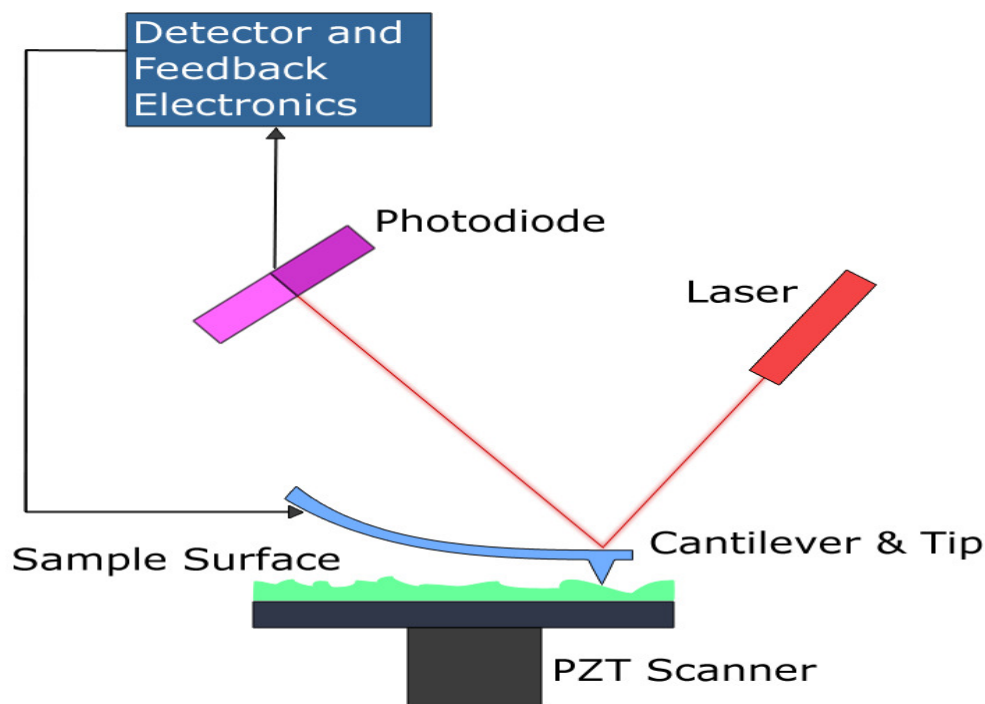


FIGURE 2.5: AFM block diagram [12].

The latter mode of operation requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope [12]. Some AFM's can accept full 200 mm wafers. The primary purpose of these instruments is to quantitatively measure surface roughness with a nominal 5 nm lateral and 0.01nm vertical resolution on all

types of samples. Depending on the AFM design, scanners are used to translate either the sample under the cantilever or the cantilever over the sample. By scanning in either way, the local height of the sample is measured. Three dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position [12].

CHAPTER 3

THE SYNTHESIS OF THERMOCHROMIC VANADIUM DIOXIDE (VO_2) THIN FILMS USING RF INVERTED CYLINDRICAL MAGNETRON SPUTTERING.

3.1 Introduction

Many transition metals when combined with oxygen form transition-metal oxides. These oxides have been the subject of experimental consideration and theoretical work for many years. They have a tendency to change their optical properties with temperature upon heating. Considering these transition metals, Vanadium dioxides (VO_2) has attracted most attention since its transition temperature is below 100°C [2]. For our purposes, the optical properties of Vanadium dioxide (VO_2) are suitable, since they change in the IR wavelength region. At room temperature, VO_2 is electrically insulating/semiconducting and highly IR transparent (see **fig.3.1**). If this material is heated above the transition temperature of 68°C , it undergoes a structural phase transition at this transition temperature; VO_2 becomes metallic electrically conducting and IR reflecting/absorbing [16].

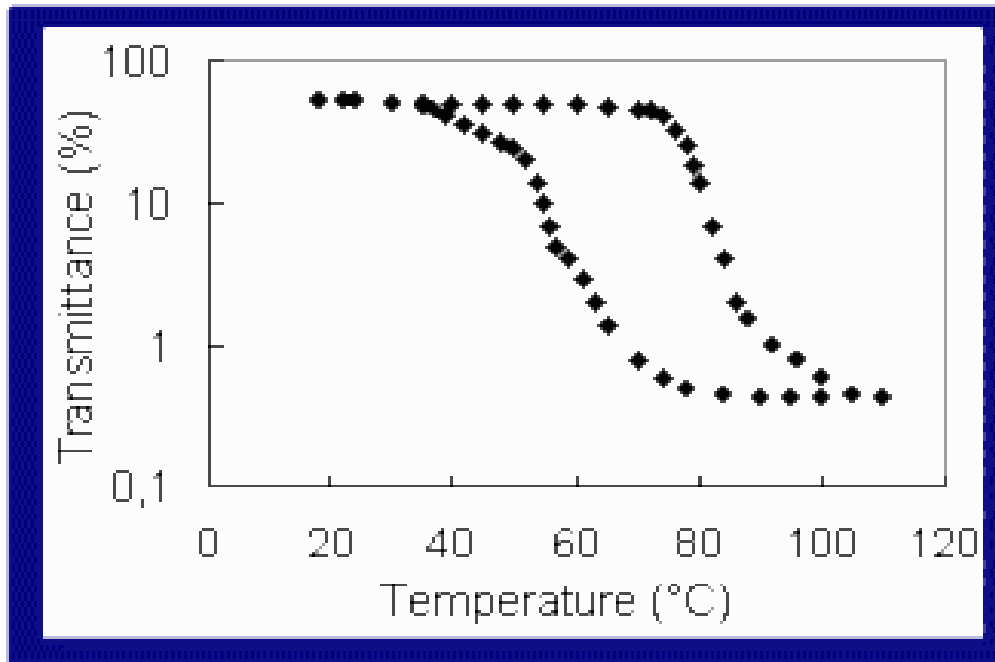


FIGURE 3.1: Optical transmittance (%) vs temperature (°C) for 300nm thick VO₂ film [2].

3.2 Sample preparation

Corning glass slides were cut into 1 cm by 1 cm squares and then cleaned by following the procedure mentioned in chapter 2. After following the cleaning procedure the samples were placed on the anode side of the sputter coat at which the temperature was raised to higher values. The chamber pressure was lowered to vacuum better than 5×10^{-6} kPa.

A gas composed of 90% argon and 10% oxygen was then allowed into the chamber.

A material which was used as a target was vanadium. The sputter chamber was then filled with a sputter gas which was argon. The glow discharge was maintained under the application of the voltage between the electrodes. The Ar⁺ ions generated in the glow discharge were accelerated towards the cathode where vanadium target was placed. The bombardment of the target by these energetic positive ions caused the surface removal of vanadium atoms. An oxygen pressure of 10^{-3} kPa was introduced inside the chamber (see **Table 3.2**). The removed vanadium atoms reacted with oxygen gas inside the chamber filled with argon. These vanadium atoms reacted with these reactive gases of oxygen forming a compound layer of VO₂ on the corning glass

substrate which was on a hot anode plate of 450°C. The other condition parameters are summarised in Table 3.2.

TABLE 3.2: Complete summary showing the conditions used in deposition of VO₂ thin film.

Parameters	Units
Vacuum	5 x 10 ⁻⁵ (mbar)
Target Vanadium metal	(99.99% purity)
Substrate temperature	450°C
Working pressure (Ar + O ₂)	8 x 10 ⁻³ mbar
Working pressure (O ₂)	10 ⁻² mbar
RF Power (forward)	70 W
RF Power (reflected)	0 W
Bias	170 V
Matching Auto (Cs)	111
Matching (Cp)	663
Deposition time	2-3 hours

3.3 Vanadium dioxide (VO₂) thin film characterization

To find out whether we had managed to synthesize VO₂ (and not one of the many other oxides) we used XRD. The existence of VO₂ film was determined by us using XRD. **Fig.3.2** shows a pattern of the film showing a polycrystalline phases of VO₂ deposited on a glass. The first strong peak appearing at $2\theta = 27^\circ$ corresponds to an oxide of vanadium phase, VO₂. Other peaks falling between 27°C and 65°C show that VO₂ is polycrystalline.

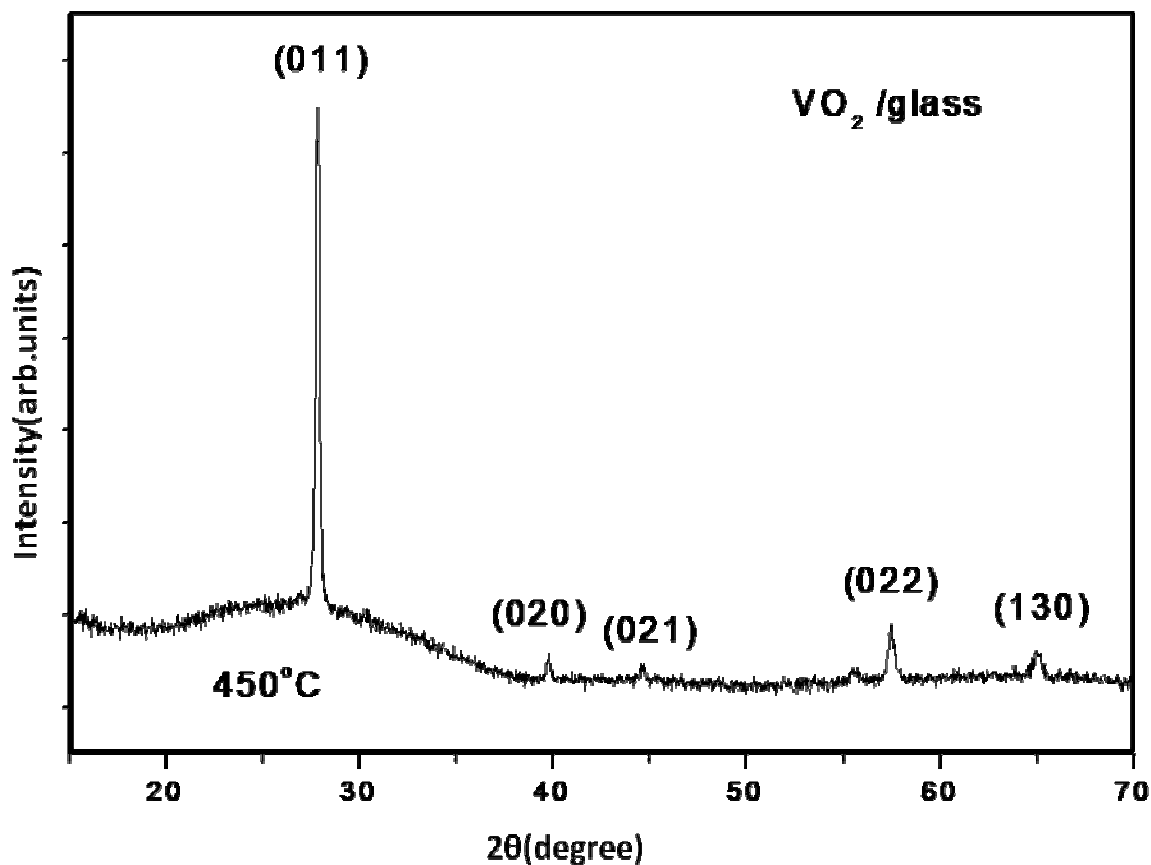


FIGURE 3.2: The XRD patterns for VO_2 film deposited on a corning glass substrate.

The transmittance of the film is measured as function of temperature using UV-Vis Spectrometer technique to further confirm the presence of the VO_2 phase.

Fig.3.3 shows the experimental transmittance curves of VO_2 film at different temperatures, when the film temperature is raised from 25°C (RT) to 95°C and subsequently reduced back to 25°C (RT).

From **Fig.3.3**, we observe a change in the transmittance as function of wavelength. The spectrum transmittance of the low-temperature semiconducting phase and high –temperature metallic phase are sharply contrasting in the infrared region, further more this VO_2 film exhibited thermochromism.

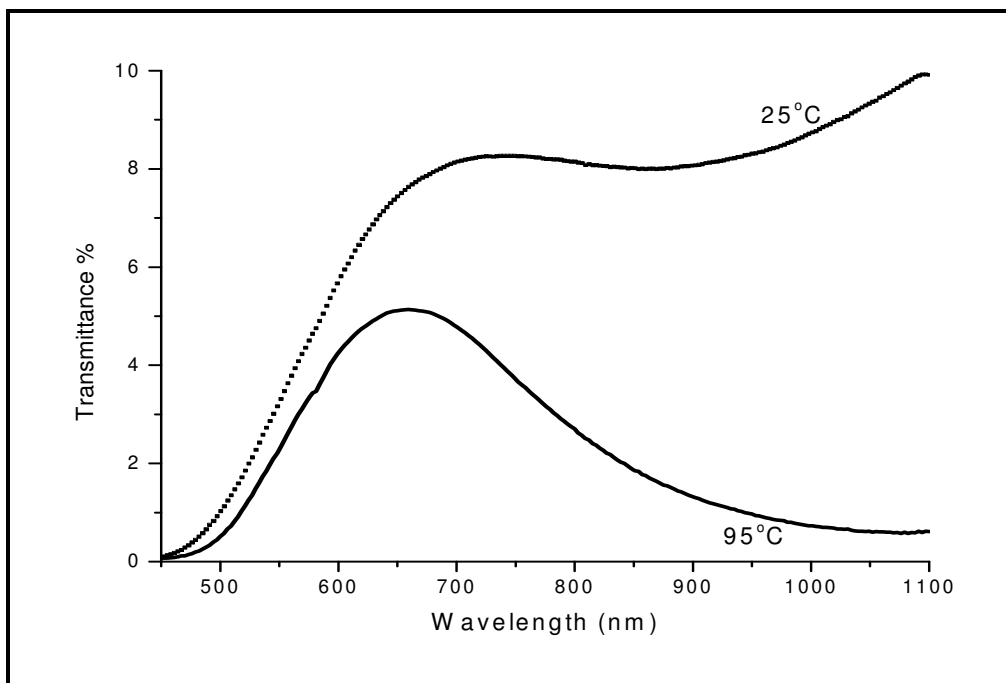


FIGURE 3.3: *Transmittance (%) vs. temperature (°C) for VO₂ film made by reactive ion sputtering.*

The transmittance of the VO₂ film on glass was observed as function of temperature as shown in **Fig.3.4**. The heating was done at the steps of 5°C, and its transmittance at various temperatures was measured at a wavelength of 1100 nm. The transition temperature of the film was in a good range reported [1-4], it should be between 60° to 70°C depending on the thickness of film. The semiconductor-to-metal transition of the deposited film was investigated using transmittance measurements as a function of temperature.

The transmittance of the film decreases with increase in temperature and shows abrupt semiconductor-to-metal phase transition. The hysteresis loop is about 10°C.

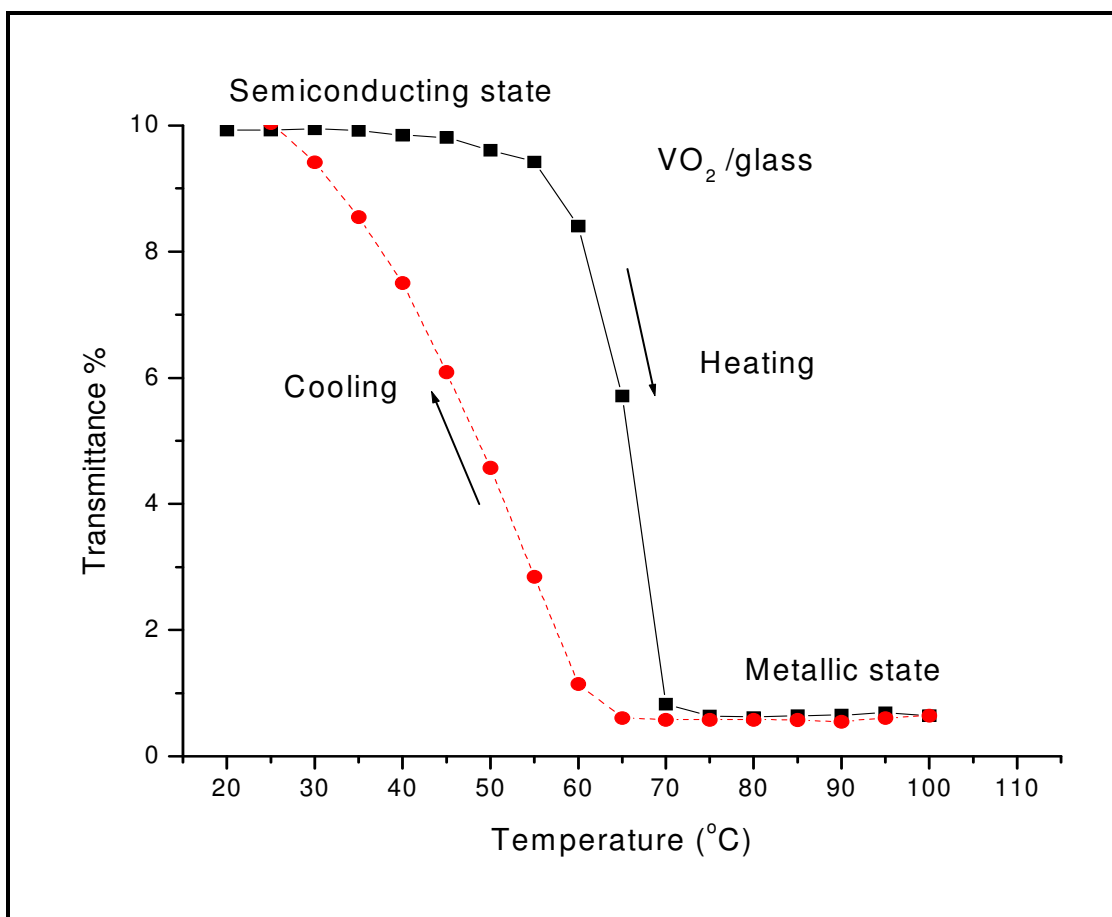


FIGURE 3.4: The transmittance (wavelength: 1100 nm) of the VO_2 film as a function of temperature. The VO_2 film was deposited on a glass.

Fig.3.5 is an image of VO_2 film measured under microscopic imaging. Using Nanoscope software the root mean square roughness (R_q) was calculated and found to be 14.3nm.

3.4 Conclusion

The VO_2 stoichiometric film was successfully deposited on a corning glass using rf-inverted magnetron sputtering under optimised conditions. Surface image and optical properties of synthesized VO_2 under optimized conditions confirm the existence of VO_2 film. The optical properties of the VO_2 nanostructure correlate with the reported [1-4]. The

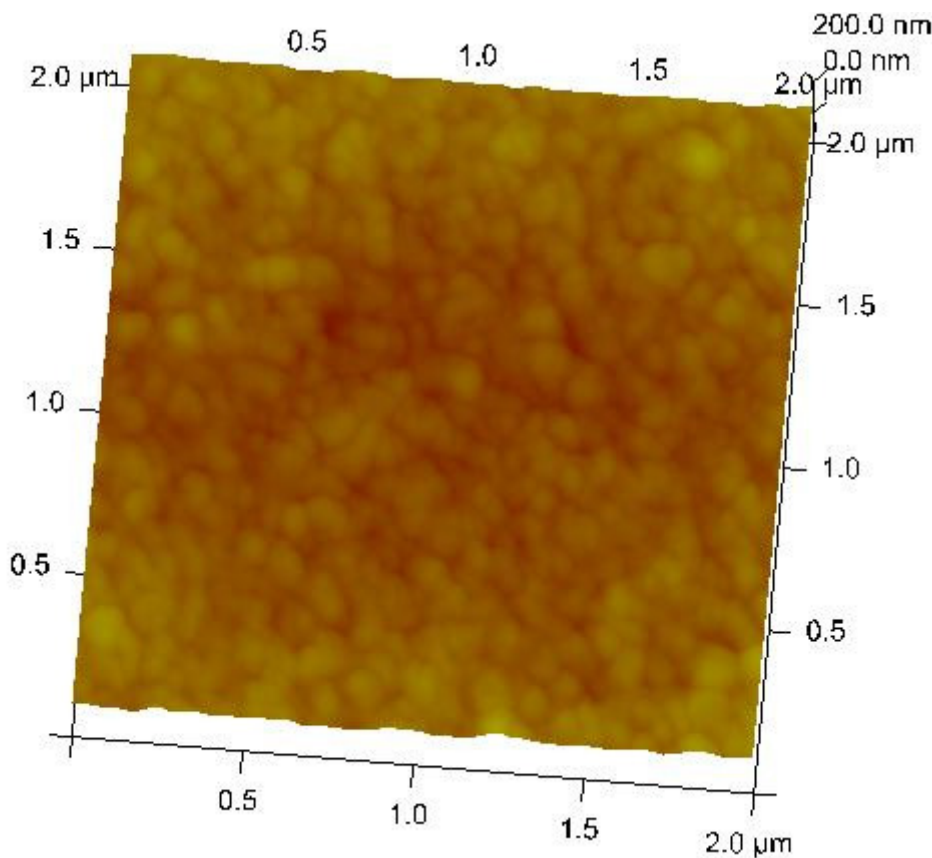


FIGURE 3.5: Atomic force microscopy of VO_2 film deposited by sputtering, with a $2.0\mu\text{m} \times 2.0\mu\text{m}$ size.

results observed allow us to conclude that the sputtered VO_2 film is the pure material of VO_2 , which then allow us to proceed under this optimized conditioned for synthesizing VO_2 film which will be used to deposit metal on top of the VO_2 such as (metal/ VO_2 /glass). The main focus of this investigation is on the synthesis of VO_2 on a glass and a metal on top of VO_2 film to check the interactions. A correlation is well established between the semiconductor-metal transition characteristic of the VO_2 film synthesized by ICMS and their sputter parameters. By controlling the sputter parameters in the ICMS film with pure VO_2 properties can be obtained. The main focus of this work is not only producing pure VO_2 phase but study the interaction of VO_2 with various metals which is explained more in details in the next chapter, which is **chapter 4**.

CHAPTER 4

EXPERIMENT ON METAL-VO₂ INTERACTION.

4.1 Introduction

Since the first observation of a metal-insulator (MI) transition in vanadium dioxide (VO₂) by Morin [15], this material has had a serious attention by many researchers [2, 4, 8, 9, and 15]. This material is being used in a wide range of technological applications such as smart window for solar energy infrared modulation, optical switches, laser protection, and optical storage [2, 7, and 16]. In this investigation various metals thin films have been deposited on VO₂ film in order to study the interaction between VO₂ and metal at the interface with the metals. The VO₂ fabricated on various metals could change completely the properties of VO₂ if it is deposited on very thin metal film [9]. On the other hand the Metal-VO₂ interaction will require a good understanding of thermodynamic stability of metals when brought in contact with VO₂ film material. The material reacts with various metals to form vanadium alloys and metal oxides which can be useful in many technological applications [30]. In this section we investigate the thermodynamic stability of various metals when in contact with VO₂.

4.2 Sample preparation

In this case we wanted to make structure of the form metal/VO₂/glass. 10 mm by 10 mm squares glasses were cut and cleaned following the sequence outlined in chapter 2. After cleaning the

samples were put into the rf magnetron sputtering chamber to deposit VO₂ on them at a substrate temperature of 450°C for some times as stated in chapter 3. After VO₂ deposition, samples with the structure VO₂/glass were mounted on sample holders then loaded in the electron beam evaporation chamber. The deposition was conducted in vacuum of better than 2×10^{-4} Pa .

A layer of 2018 Å of Pt was deposited on VO₂/glass using evaporation technique in vacuum. The evaporation rate was maintained at about 1.8 Å/s. A layer of Pd was also deposited on top of VO₂. The deposition rate was maintained at 3.0 Å/s. A thick layer of 3650 Å of Hf was deposited on a structure VO₂/glass under the vacuum of about 2×10^{-4} Pa . A 2094 Å layer of Co was electron-gun on top of VO₂ at a rate of about 3.0 Å/s. The evaporation was done under vacuum better than 2×10^{-4} Pa . A 1380 Å of Al was evaporated by means of electron gun on top of VO₂ film that was sputtered on a glass. The evaporation rate was maintained at about 1.2 Å/s. In case of Ni, a 2022 Å layer was electron-gunned on top of VO₂ at a rate of 2.4 Å/s. The vacuum was better than 2×10^{-4} Pa .

The samples were put in different bunch since the evaporation technique can only evaporate three different materials simultaneously. The samples after evaporation were left under vacuum and allowed to cool for about 2 hours or more. After deposition of the metal the Metal/VO₂/glass samples were annealed in an oil free vacuum system, with vacuum better than 10^{-4} Pa. The Metal/VO₂/glass samples were then loaded in quartz boats and annealed at preset temperatures under vacuum for different time intervals. The vacuum was better than 10^{-5} Pa. Rutherford Backscattering Spectrometry was used to analyse the samples. The thickness of each was determined using Rutherford Universal Manipulation Program (RUMP). X-Ray Diffraction (XRD) was also used to identify compound phases.

4.3 Results

4.3.1 Pd-VO₂.

A Palladium layer was deposited by electron beam on a VO₂/glass sample at 3.0 Å/s rate. The vacuum was maintained at about 2×10^{-4} Pa during deposition. The deposited Pd layer was 2070 Å in thickness. The samples were removed from the evaporation chamber and were loaded

into boats placed in vacuum for annealing. The virgin sample was kept under vacuum while the other was annealed at 700°C for one hour. Rutherford Backscattering Spectrometry (RBS) was used to analyse the samples. The thickness was determined by using RUMP program.

Fig.4.4.1 is a RBS spectrum of the Pd as deposited (i.e. no heat) sample and one annealed at 700°C for 1 hour. The as-deposited sample shows no interaction between VO₂ and Pd, it also shows no signs of oxidation. The sample annealed at 700°C looks similar to the unannealed sample. We conclude therefore from RBS results that there is no interaction between Pd and VO₂ up to temperatures of 700°C.

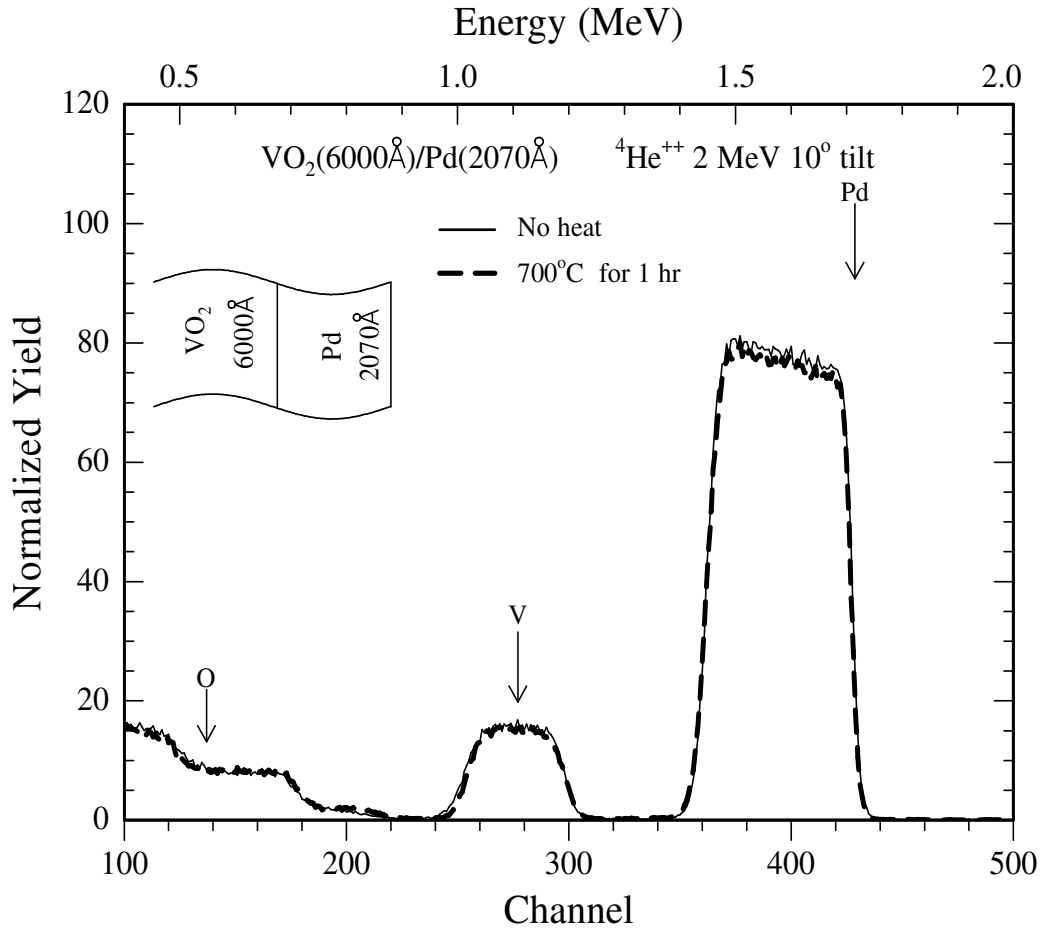


FIGURE 4.4.1: There are two samples in the Backscattering spectra of VO₂(6000Å)/Pd(3280Å). The as-deposited sample and the one sample annealed at 400°C for 30 minutes. The virgin or as-deposited sample shows no reaction between VO₂ and Pd. The RBS spectrum of the annealed sample look similar to that one of the virgin sample therefore these RBS result tells that no reaction between VO₂ and Pd.

A 2018Å layer of Platinum (Pt) was electron-gun evaporated on to VO₂ (3000Å)/glass at a rate of 1.8Å/s. The vacuum was oil free and better than 10⁻⁷kPa. One of the Pt-VO₂ samples was annealed at a temperature of 700°C for 1 hour while the other one was unannealed sample and kept in vacuum to avoid any possible oxidation.

4.3.2 Pt-VO₂.

RBS results for the as deposited Pt sample and the other sample annealed at 700°C for 1 hour are in **Fig.4.4.2**.

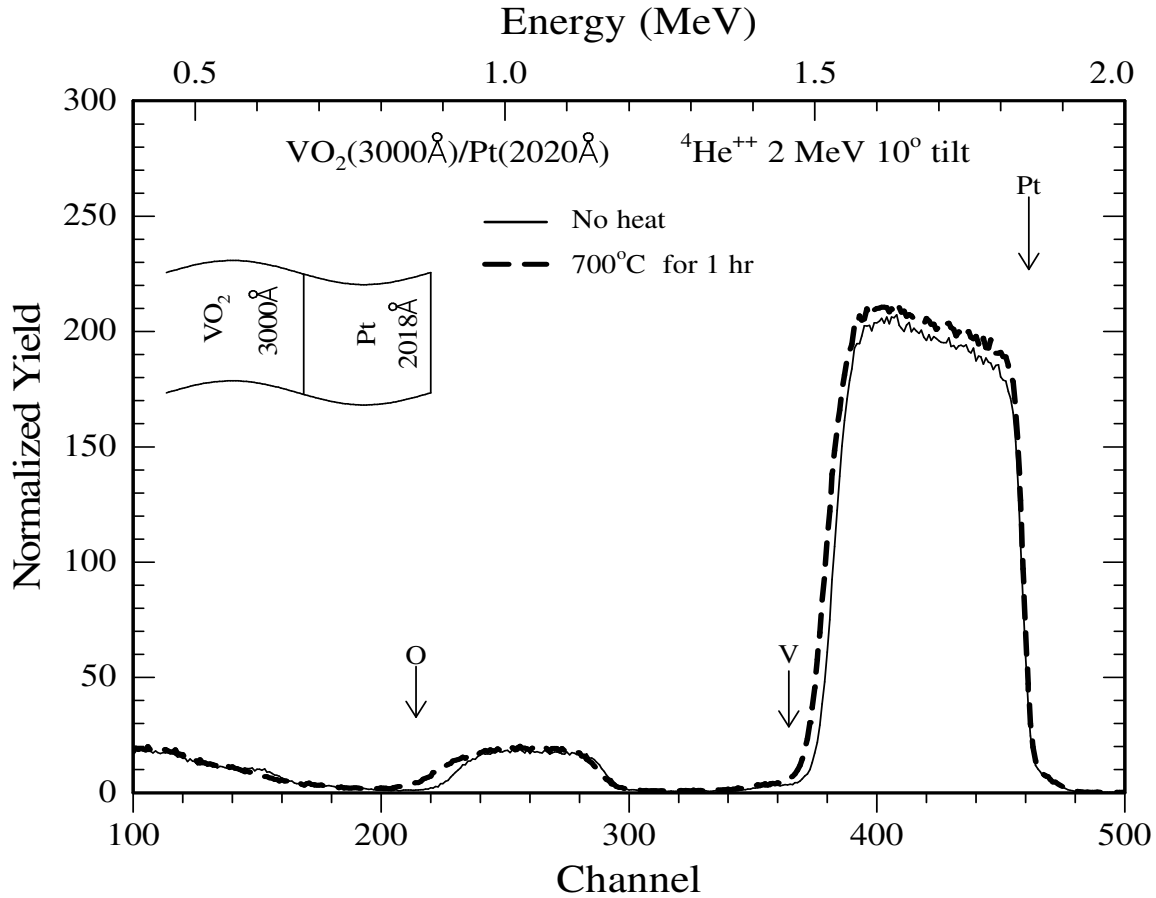


FIGURE 4.4.2: Backscattering spectra of VO₂ (3000Å)/Pt (2018Å)/glass samples as-deposited and annealed for 1 hour. The as-deposited sample and the annealed sample show no interaction at temperature 700°C.

These results show an RBS spectrum of the virgin sample (i.e no heat) and the other sample heated at 700°C for 1 hour. The virgin sample shows no interaction between VO₂ and Pt also

shows no signals of oxidation. The thickness is different but the spectra look similar. There is therefore no interaction between VO_2 and Pt on these samples according to our RBS.

4.3.3 Ni- VO_2 .

The results in **Fig.4.4.4** show an RBS results of the as-deposited Ni sample and one annealed at 700°C for 1 hour in a vacuum better than $1.33 \times 10^{-5} \text{ Pa}$. The as-deposited sample shows no reaction between Ni and VO_2 . The Ni signal of the annealed sample does not match at the Ni/ VO_2 interface; hence this signal shows the partial peeling in VO_2 and Ni. The Nickel layer which was covering the VO_2 layer on top of a corning glass was no longer covering the whole surface due to the peeling in some of the spot and showing off the VO_2 layer underneath. This condition is shown in **Fig 4.4.3**. This observation has no evidence of any reaction between Ni and VO_2 , but show that Ni peels when in contact with VO_2 at higher annealing temperatures.

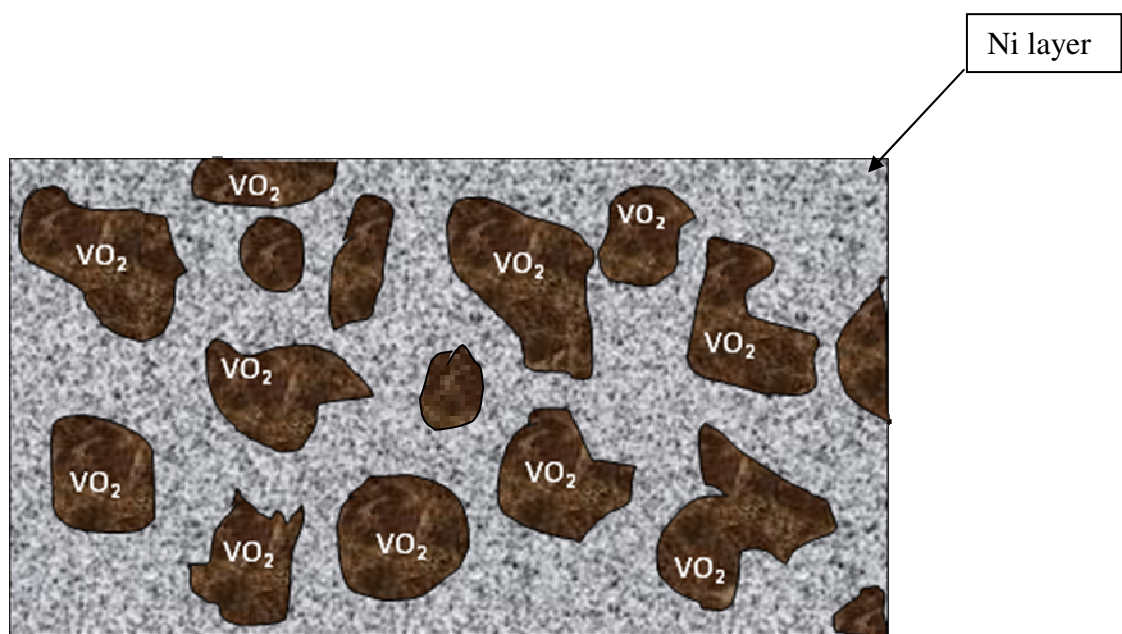


FIGURE 4.4.3: A drawing representing a partially peeled Nickel layer on top of VO_2 layer that was on glass substrate. The Ni layer has peeled on some spot thus exposing VO_2 layer when annealed at higher temperature of 700°C .

RBS results for Ni samples annealed at 700°C for 1 hour show that no reaction between VO_2 and Ni (see **Fig.4.4.4**). Hence the experimental results support the theoretical predictions of no interaction between Ni and VO_2 .

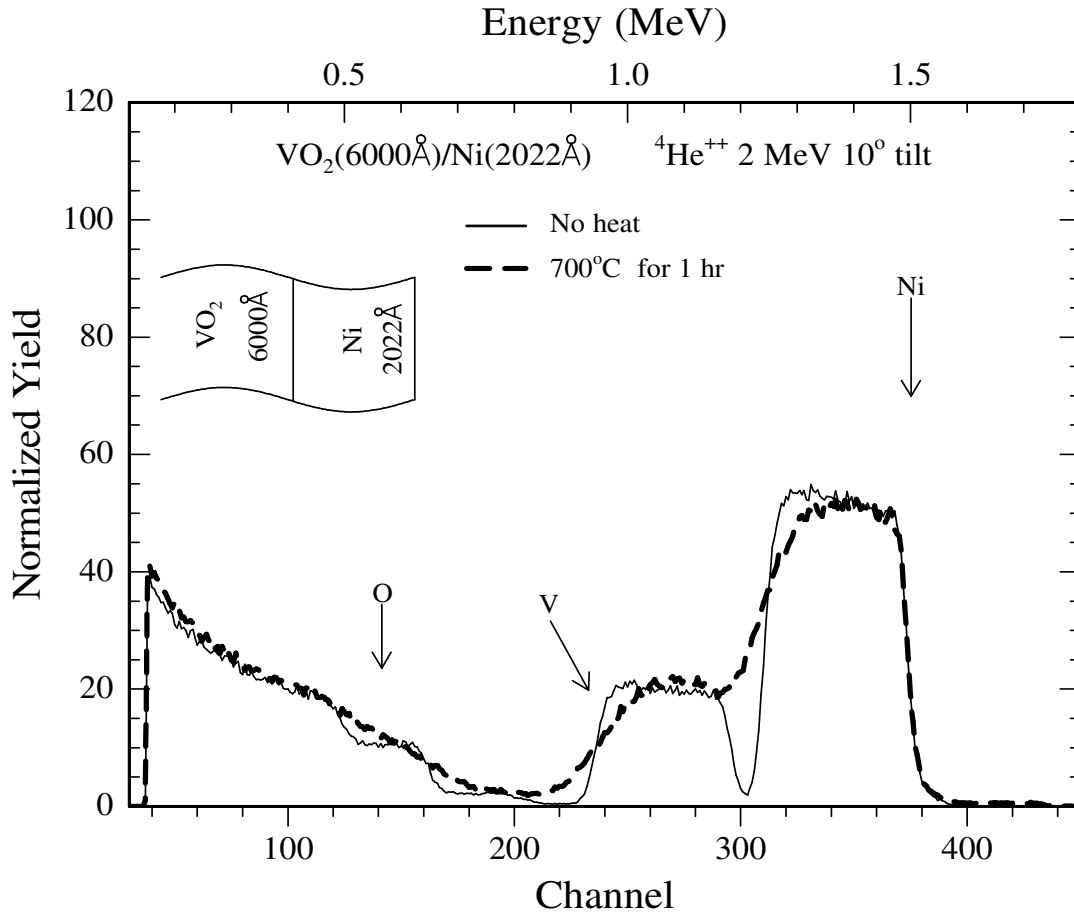


FIGURE 4.4.4: The RBS spectra of samples whose structure is Ni (2022Å)/VO₂ (6000Å)/glass showed that there was no interaction. There are two samples, the as-deposited sample, the sample annealed for 1 hour at 700°C. The spectrum of the as-deposited sample shows no reaction between VO₂ and Ni.

4.3.4 Co-VO₂.

A 2094Å layer of Cobalt was electron-beam deposited on a structure of VO₂ (5050Å)/glass. The pressure in the vacuum chamber was approximately 2×10^{-7} kPa during deposition and the rate was 3.0 Å/s. One sample was taken to vacuum annealed up to temperature of 700°C for 1 hour whilst the other sample was kept under vacuum as a virgin sample. **Fig.4.4.5** is an RBS result that was carried out for both as-deposited and the annealed samples. The as-deposited sample shows no interaction between VO₂ and Co, it also shows no signal of oxidation. The 700°C annealed sample does not exactly match that of virgin sample at the Co/VO₂ interface. This is the same case as in Nickel (Ni) peeling off, Co and Ni are in the same group in their periodic table

so similar behaviour was expected in this case. Co partially peeled when heat treated to higher temperatures (i.e. 700°C) exposing VO₂ layer which was underneath the Co layer (see **Fig.4.4.3**).

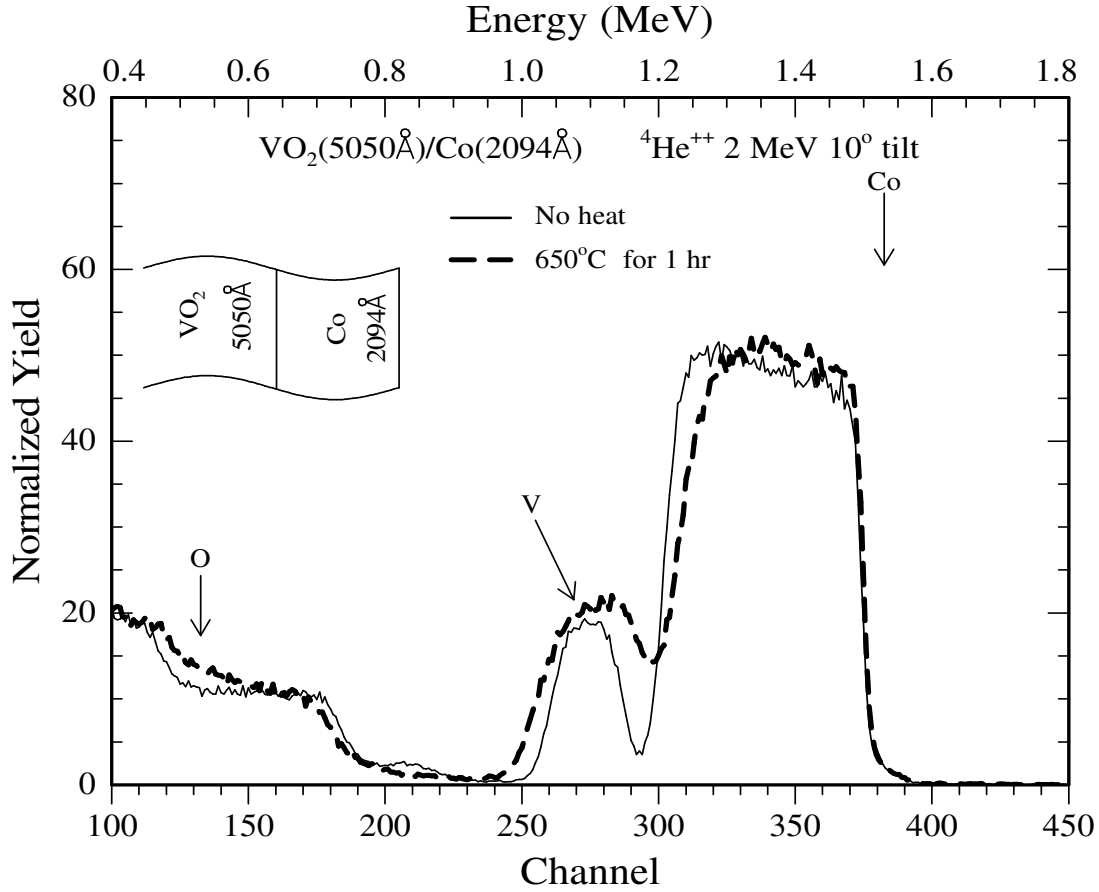


FIGURE 4.4.5: RBS spectra for samples of this structure Co (2094Å)/VO₂ (5050Å)/glass. Two samples of such structure were available, with one kept as a virgin sample whilst the other one was annealed for 700°C for 1 hour. The virgin sample shows no sign of interaction and oxidation.

4.3.5 Hf-VO₂.

RBS results for the Hf virgin sample and two samples annealed at 400°C and 450°C are shown in **Fig.4.4.6**. These results show RBS spectrum of the as-deposited Hf sample and the two other samples, one annealed at 400°C and the other one annealed at 450°C for 45 minutes. The as-deposited sample shows no signal of interaction between Hf and VO₂. The RBS spectrum for the sample annealed at 400°C for 45 minutes shows that V atoms has diffused into the Hf layer forming a phase at the interface. This might be possible partly due to oxidation of Hf and due to

the formation of the new phase between Hf, O and V. This can be observed by comparing the annealed sample with the virgin sample. The spectrum of the annealed sample at 400°C has been reduced and its width has been broaden compared to that of as-deposited (i.e no heat) sample. The V signal shows the signal of the two annealed samples match but their widths are reduced. This is due to the migration of V atoms to Hf region and O atoms from VO₂ are present at the interface. The RBS spectrum for the sample annealed at 450°C for 45 minutes, its height is also reduced and its width is broadened due to the oxidation of Hf. Therefore these samples show the presence of O, V and Hf at the interface. No clear shoulder developed on the Hf signal to allow us to guess stoichiometric ratios for known equilibrium phases. Using the RUMP simulation and RBS we can conclude that VO₂ is unstable when in contact with Hf and does react with it at about 400°C.

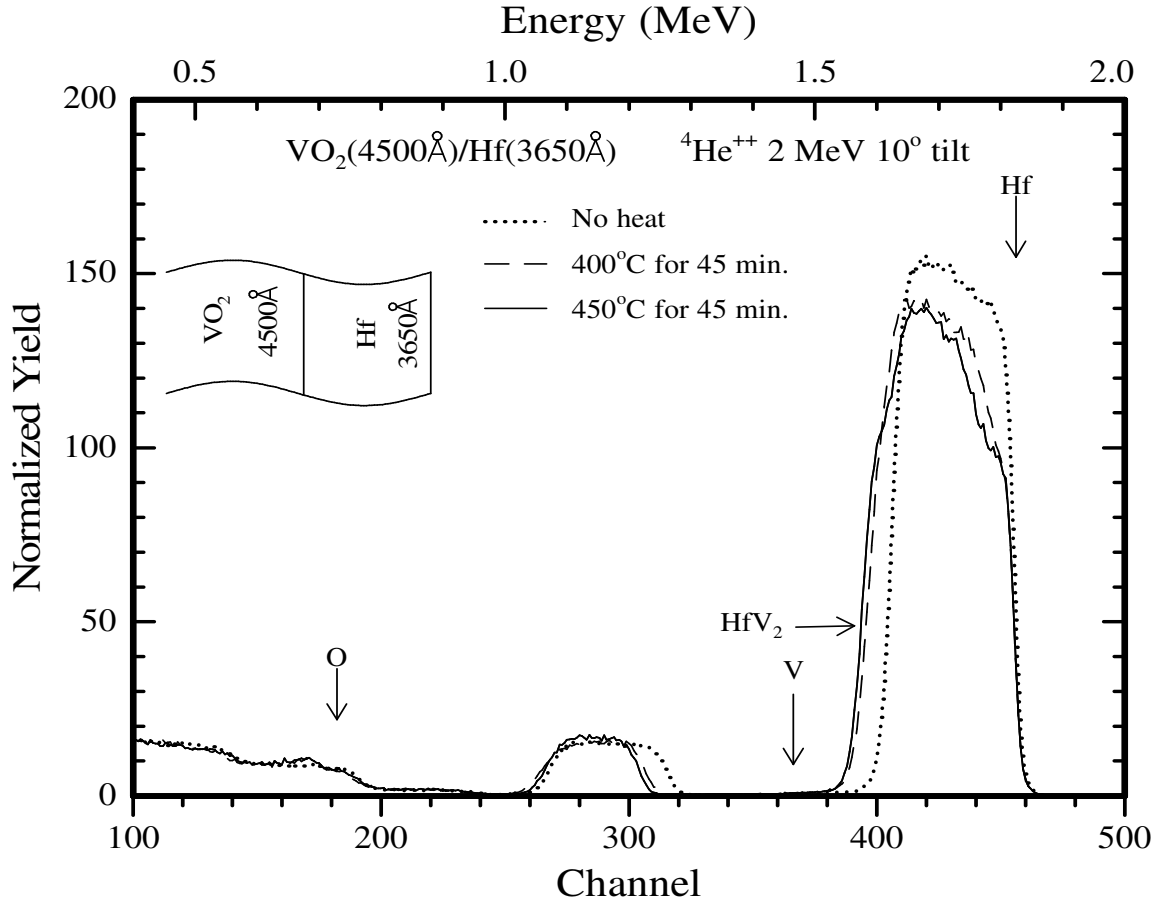


FIGURE 4.4.6: There are three samples in the Backscattering spectra of VO₂ (4500Å)/Hf (3650Å). The as-deposited sample and the other two samples annealed at 400°C for 45 minutes and one annealed at 450°C for the same time shows that there is reaction while the virgin or as-deposited sample shows no reaction between VO₂ and Hf.

4.3.6 Al-VO₂.

Fig. 4.4.7 shows results of Rutherford Backscattering Spectrometry (RBS) for Al electron-beam deposited under the vacuum better than 2×10^{-7} kPa at a rate of 1.2 Å/s. Two samples were synthesized due to the difficulty in getting pure VO₂ film. One sample was treated as a virgin and kept under vacuum to prevent any possible oxidation while the other sample was put in a boat and loaded in a furnace in order to anneal at temperature of 530°C for 2 hours. The virgin shows no sign of interaction. The RBS spectrum of the sample annealed at 530°C for 2 hour shows some effect in the RBS spectrum when comparing it to the unannealed. The heights of Al and V have been reduced. This might be because of oxidation and/or loss of material probably to the formation of some volatile phase of AlVO₂ at the interface of Al/VO₂ during annealing.

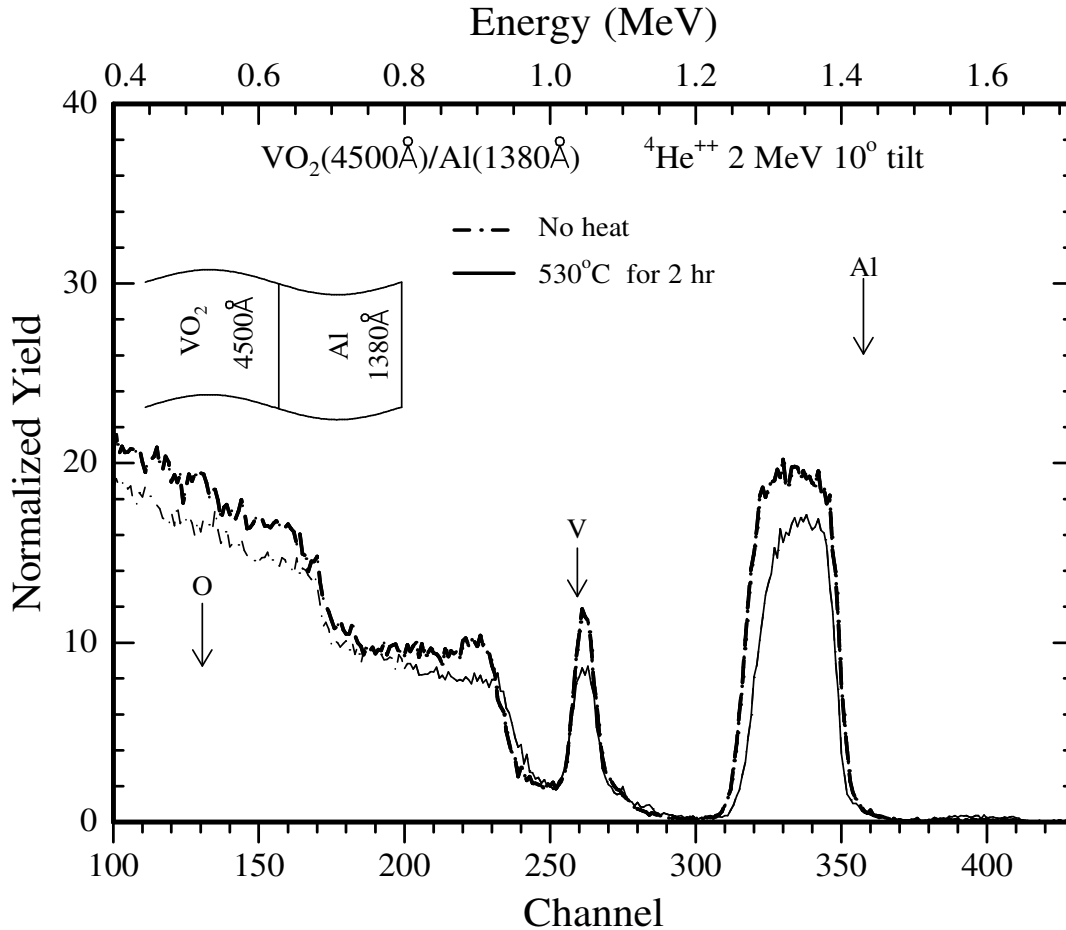


FIGURE 4.4.7: RBS spectra for samples with same structure of Al (1380Å)/VO₂ (4500Å)/glass. One sample was kept under vacuum as a reference as that sample shows no signal of interaction at room temperature while the other one was annealed at 530°C under vacuum in a furnace.

Fig.4.4.8. shows an X-Ray Diffraction patterns for samples annealed in vacuum at various temperatures. These samples have the profile Hf(3650Å)/VO₂(4500Å)/ glass before annealing. The as-deposited sample shows that Hf crystallizes upon deposition and the well shows the presence of the monoclinic VO₂. Within the limits of the sensitivity of X-Ray Diffraction (XRD) the as-deposited sample shows no oxidation peaks in agreement with our RBS spectrum for the as-deposited sample which shows no oxidation took place. The sample annealed at 400°C shows the growth of HfV₂ peak which left some materials of VO₂ and Hf unreacted at the interface. When the temperature was raised by 50°C from 400°C to 450°C, the sample shows the strong peak of HfV₂ and also some small peaks of HfO₂, leaving some of the materials unreacted.

4.4 Summary and Conclusion

A thermodynamic stability of VO₂-metal thin films interaction was investigated. Lately some work has been done and reported on VO₂ on top of a metal buffer layer to investigate the effect of the buffer layer on the properties of VO₂ [9]. VO₂ was deposited on various metals in that case. In this investigation a metal was deposited on top of a VO₂ film which was sputtered on a coming glass. The purpose of depositing a metal on top of VO₂ thin film was to investigate the interaction between metal and VO₂ at an interface of metal/VO₂. VO₂ is one of the thermochromic oxides material which undergoes a transition at low temperature of 68°C [1-4]. VO₂ when allowed to interact with various metals may result in a reaction. When a reaction occurs, a product which can find its uses in many technological applications may be formed. In the case of the metals (Pt, Co, Ni, and Pd), no reaction with VO₂ occurred for temperature up to 700°C for 1 hour. Heats of reaction were calculated for these metals and VO₂ from thermodynamics (see **chapter 1**). For metals that do not react it was found that their heats of reaction are positive which tells us that they are stable when in contact with VO₂ and therefore their reaction may not proceed to the right and form products. So using thermodynamics alone we did not expect a reaction between these metals and VO₂. From experimental observation one would conclude that Pt, Co, Ni, and Pd do not react with VO₂ and using thermodynamics alone one would also conclude that thermodynamics predictions agree with our experimental results.

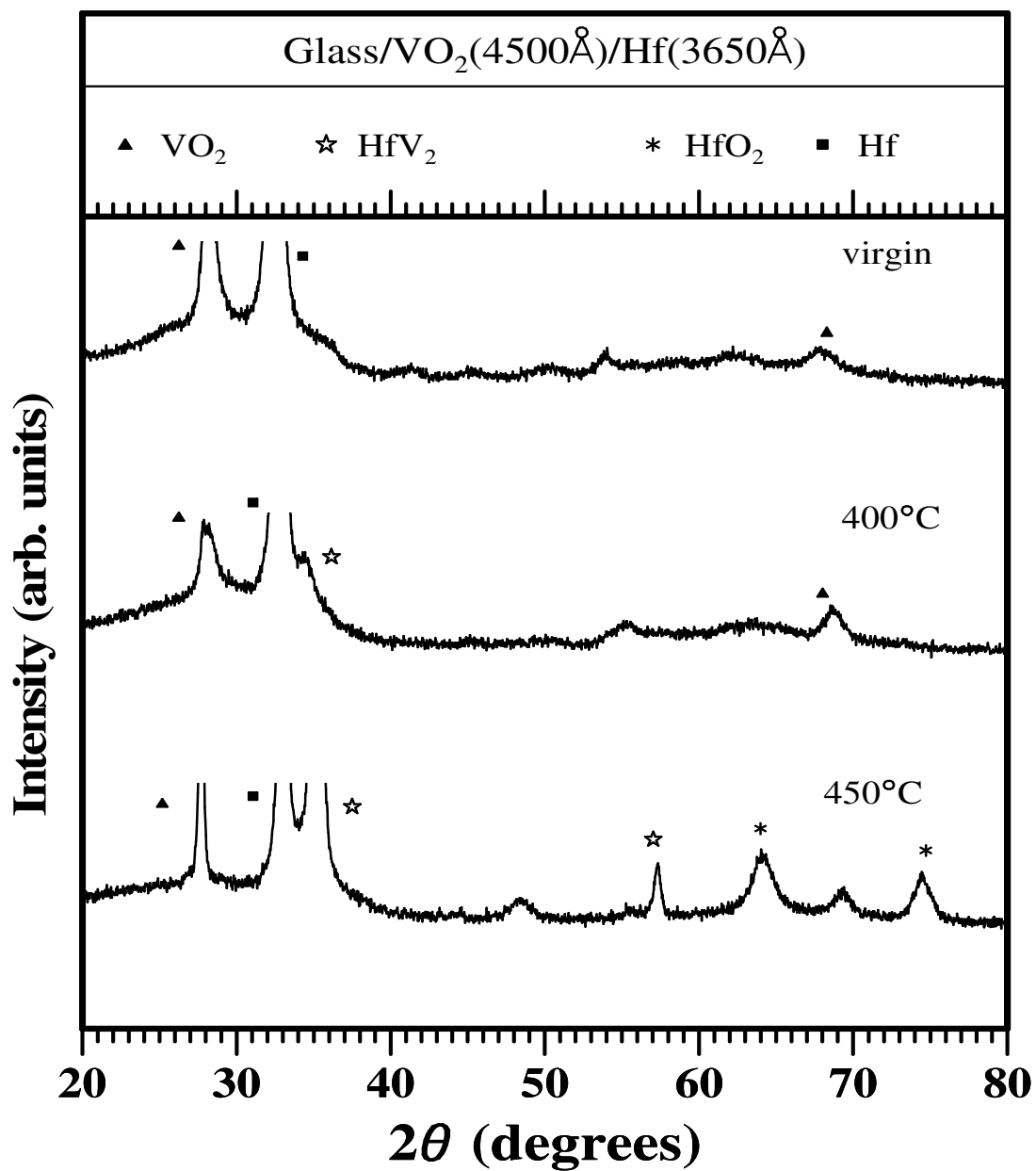


FIGURE 4.4.8 : The X-Ray Diffraction (XRD) patterns for Hf(3650Å) /VO₂(4500Å) /glass samples. There are three samples one used as reference or virgin, the other ones annealed at higher temperatures. The annealed samples, one was annealed at 400°C and the other at 450°C for 45 minutes. The as-deposited sample shows the presence of VO₂ and Hf. The spectrum annealed at 400°C showed the presence of VO₂, Hf, and HfV₂. The spectrum annealed at 450°C shows the presence of VO₂, Hf, HfV₂, and HfO₂.

RBS results show that Hf and Al do react with VO_2 and form compounds, Al formed only Al_2O_3 . The Rutherford Universal Manipulation Program (RUMP) was used to check for the presence of compound phases. The presence of these compound phases was confirmed using X-Ray Diffraction (XRD) for those metals that react with VO_2 .

CHAPTER 5

PREDICTION OF METAL-VO₂ INTERACTION.

5.1 Introduction

So much work has been done already on metal-metal systems and lots of models have been developed to predict possible reactions and compound phases at the interface. Pretorius *et al* [21] suggested that a reaction between an oxide and a metal usually results in strong adherence between a metal and the oxide while in cases where there is no reaction; metal layers are seen to peel upon annealing. A uniform stable interface is ideal for coating VO₂ with metals. Therefore knowledge of all reactions and compound phases at the interface is of great importance to the material scientists. In this work experimental observations are compared to the theoretical predictions in order to draw general conclusions at the end of our work. This undertaking however can be shortened by supplementing experimental observations with theoretical predictions which are discussed in this chapter.

5.2 Calculated heats of reaction

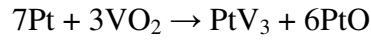
Suppose a reaction between a metal thin film with VO₂ resulting in the formation of a metal oxide and a Vanadium alloy may be written as:



Where x and y are the atomic concentrations. M is the metal and it is assumed that the resulting products are Vanadium alloy and a metal oxide. The reaction considered happen at constant temperature and pressure, where the change in Gibbs's is given by

$$\Delta G = \Delta H - T\Delta S \quad (5.2)$$

where ΔH is the change in enthalpy or heat of reactions. $\Delta S \approx 0$ since it is assumed that both reactants and products are solids. ΔG is therefore approximated to change in enthalpy or heat of reaction. If the enthalpy of reaction is negative, then the reaction between VO_2 and the metal is thermodynamically possible. Let us take a reaction between VO_2 and Pt as an example to form PtV_3 and PtO . Values of standard heats of formation (ΔH) of various metal oxides and Vanadium alloys are given in APPENDIX. The heat of reaction in this instance is calculated as follows:



$$7(0) + 9(-237.8) \rightarrow 4(-43.78) + 12(-35.6)$$

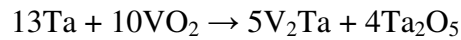
$$\Delta H_R = \frac{[4(-43.78) + 12(-35.6)] - [9(-237.8)]}{16}$$

$$\Delta H_R = +95.6 \text{ kJ/ (mol.at)}$$

Working out the other possibilities for this system, it is found that all ΔH_R are positive.

This means that Pt does not react with VO_2 . Next consider the reaction between VO_2 and Ta to form V_2Ta and Ta_2O_5 . As before the values of standard heats of formation (ΔH) of various metal oxides and Vanadium alloys are also given in **APPENDIX**.

The heat of reaction in this system will be calculated as follows:



$$13(0) + 30(-237.8) \rightarrow 15(-1.33) + 28(-292.3)$$

$$\Delta H_R = \frac{[15(-1.33) + 28(-292.3)] - [30(-237.8)]}{43}$$

$$\Delta H_R = -24.89 \text{ kJ/ (mol.at)}$$

There was only one compound phase for this system as calculated above with negative heat of reaction. This means that Ta does react with VO₂.

The values of heat of reaction calculated in this manner are shown in **Table 5.1** for various interactions between VO₂ and some metals. All values of standard heat of formation (ΔH) of various metal oxides and Vanadium alloys that appear in this table were obtained from **APPENDIX**.

TABLE 5.1: *Calculated heat of reaction for metal-VO₂ interactions.*

Element	Vanadium alloy	Oxides	ΔH_R kJ/(mol.at)	Element	Vanadium alloy	Oxides	ΔH_R kJ/(mol.at)	
Pd	Pd ₃ V	PdO	51.40	Al	Al ₃ V	Al ₂ O	35.6	
	Pd ₂ V		59.30			AlO	99.8	
	PdV ₃		174.40			Al ₂ O ₃	-68.3	
Ni	Ni ₃ V	NiO	19.81	Al ₂₁ V ₂		Al ₂ O	20.4	
		Ni ₂ O ₃	42.70			AlO	51.5	
	Ni ₈ V	NiO	12.20				Al ₂ O ₃	-68.3
		Ni ₂ O ₃	25.40	Al ₄₅ V ₇		Al ₂ O	26.55	
	Ni ₂ V	NiO	23.14			AlO	69.9	
		Ni ₂ O ₃	50.00			Al ₂ O ₃	-46.52	
	NiV ₃	NiO	39.50	Al ₂₃ V ₄		Al ₂ O	27.99	
		Ni ₂ O ₃	78.30			AlO	74.3	
Hf	HfV ₂	HfO ₂	-96.85			Al ₂ O ₃	-49.60	
Pt	Pt ₃ V	PtO	50.4	Al ₈ V ₅		Al ₂ O	42.00	
		Pt ₃ O ₄	61.90			AlO	121.80	
		PtO ₂	58.8			Al ₂ O ₃	-83.56	
	Pt ₂ V	PtO	58.2	Zn	V ₄ Zn ₅	ZnO	-2.66	
		Pt ₃ O ₄	72.03			VZn ₃	ZnO	-2.60
		PtO2	69.22			VZn ₁₆	ZnO	-0.998
	PtV	PtO	72.4	Sn	Sn ₃ V ₂	SnO ₂	17.2	
		Pt ₃ O ₄	90.10			SnO	17.00	
				Cont....				

Element	Vanadium alloy	Oxides	ΔH_R kJ/(mol.at)	Element	Vanadium alloy	Oxides	ΔH_R kJ/(mol.at)
		PtO ₂	88.5		SnV ₃	SnO ₂	26.5
	PtV ₃	PtO	95.6			SnO	24.6
		Pt ₃ O ₄	118.1				
		PtO ₂	119.5				
Co	Co ₃ V	CoO	22.6				
		Co ₃ O ₄	28.11				
	CoV ₃	CoO	41.39				
		Co ₃ O ₄	51.92				
Rh	Rh ₃ V	Rh ₂ O	41.1				
		RhO	52.6				
		Rh ₂ O ₃	50.88				
	Rh ₅ V ₃	Rh ₂ O	48.2				
		RhO	206.75				
		Rh ₂ O ₃	63.3				
	RhV	Rh ₂ O	54.3				
		RhO	232.5				
		Rh ₂ O ₃	74.3(TETR./ORTHO)				
	RhV ₃	Rh ₂ O	66.1				
		RhO	270.99				
		Rh ₂ O ₃	95.70				

5.3 Measured metal-VO₂ interactions

A study of a solid interaction between VO₂ and e-gun deposited thin metal films of metals was conducted. All depositions were conducted in vacuum. The samples were annealed in vacuum at various temperatures for time up to 2 hours. They were then characterised using RBS and XRD. The study reveals that some metals react with VO₂ and some do not. The results obtained in this work on the interaction of metals with VO₂ are summarised in **Table 5.2**.

After successfully synthesizing the VO₂ film on a corning glass, the samples with structure glass/VO₂/metal were characterized. The metals which were deposited on glass/VO₂ were Pd, Ni, Hf, Pt, Co, and Al.

In case of Pd metal, we found that Pd does not react with VO₂ when annealed in vacuum for temperature up to 700°C for 1 hour. Thin film of Pt metal was deposited on corning glass substrates. All the annealing experiment was conducted under a vacuum at temperature similar to the one used under Pd annealing of 700°C for 1 hour. Pt metal was found not react with VO₂. We also found that the Co and Ni metals which are in the same group in the periodic table of elements have a strange behaviour. These metals were annealed under vacuum at a temperature up to 700°C. Experimental results showed no signal of reaction between Ni and Co when each is in contact with VO₂, but the Ni metal film and Co film peel when annealed at higher temperatures up to 700°C. We found that Hafnium (Hf) reacts in contacts with VO₂. The resulting compound phases were identified using XRD in the reacted region as HfO₂, and HfV₂.

TABLE 5.2: *Metal-VO₂ interactions.*

Metal	Reaction
Al	Yes
Co	No
Hf	Yes
Ni	No
Pd	No
Rh	No
Sn	No
Ta	Yes
Pt	No
Zn	Yes

5.4 Comparison between experimental results and calculations.

The reactants investigated were all in solid state and all reactions took place in constant temperature and pressure, therefore the change in Gibb's free energy may be approximated by

$$\Delta G \approx \Delta H$$

Since the entropy S of the Gibb's free energy in this case is equal to zero (see **chapter 1**).

Pd-VO₂

The calculated ΔH_R values for all possible Pd-VO₂ interaction may be obtained from **Table 5.1**. The heat of reaction is positive for all possible Pd-VO₂ interactions which mean that the reaction

is not thermodynamically favoured and can therefore not occur on its own. This means that Pd is not expected to react with VO₂ at constant temperature and pressure.

In the as deposited sample of Pd and VO₂ no interaction between Pd and VO₂ is observed and RBS results for Pd samples annealed at temperature of 700°C for one hour show no reaction between Pd and VO₂. The sample annealed at 700°C looked similar to the as-deposited (no heat) sample. The experimental results for Pd are in good agreement with theoretical predictions since the heats of reaction are positive for the formation of these products (see **Fig.4.4.1**).

Pt-VO₂

Using the values of the standard heat of reaction (ΔH°) as listed in **APPENDIX**, the heats of reaction (ΔH_R) for all the combinations of the vanadium-Pt and oxides of Pt were calculated and are given in **Table 5.1**. The calculated heats of reaction for all possible combination are positive. According to the thermodynamics, none of these reaction products will be formed spontaneously.

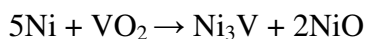
RBS spectrum of the Pt (3000Å)/VO₂ (2018Å)/glass system annealed at temperatures up to 700°C for one hour show no reaction between Pt and VO₂. Hence this observation made on the RBS

spectrum is in agreement with the theoretical predictions which have positive values of (ΔH_R) for the formation of these products (see **Fig.4.4.2**).

Ni-VO₂

The calculated heat of reaction for all possible Ni-VO₂ interactions resulting in the formation of Vanadium-Nickel alloys and oxides of Ni may be obtained from **Table 5.1**.

Consider the following reaction:



The calculated heat of reaction obtained from **Table 5.1** is equal to +19.81 kJ/ (mol.at). The heat of reaction is positive which indicates that the reaction is not thermodynamically favoured and will therefore not occur spontaneously. Considering all the reaction for Ni-VO₂ system the heats of reaction are all positive, which means Ni is not expected to form any reaction with VO₂.

Co-VO₂

The calculated heats of reaction for all possible Co-VO₂ interactions are summarised in **Table 5.1**. The heat of reaction was found to be positive for all possible Co-VO₂ interactions, which suggest that the reaction between Co and VO₂ is not thermodynamically favoured and can therefore not occur on its own.

RBS results of the Co sample annealed at temperature up to 700°C shows no reaction between Co and VO₂. Then the experimental results for Co are in agreement with theoretical predictions with the heats of reaction are positive for the formation of these products (see **Fig.4.4.5**).

Hf-VO₂

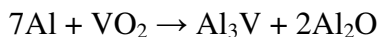
The calculated values of the heat of reaction for all possible Hf-VO₂ interaction resulting in the formation of Vanadium-Hafnium alloy and oxide of Hf may be obtained from **Table 5.1**. The heat of reaction was found to be negative for all possible Hf-VO₂ interactions, which means that the reaction between Hf and VO₂ is thermodynamically favoured and can therefore occur on its own.

Fig.4.4.6 shows an RBS spectrum of the Hf as-deposited sample and the other two samples annealed at 400°C and 450°C for 45 minutes. The as-deposited sample shows no interaction between VO₂ and Hf. The RBS spectrum for the sample annealed for 45 minutes at 400°C shows that V atoms has migrated to Hf layer and its height is reduced as well as width has broadened. Once the temperature has been increased from room temperature (25°C), the spectrums get reduced and width broadened because some of Hf gets oxidized and new phases might form between Hf, V and O. The virgin sample RBS spectrum acts as a reference for the RBS of the

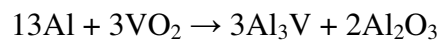
annealed samples. This can be seen from the sample annealed at 400°C. Its height is reduced compare to the height of the virgin sample. The RBS spectrum of the sample annealed at 450°C looks almost similar to the RBS spectrum of the sample annealed at 400°C. This sample shows the presence of V and O in the Hf layer. Considering from the higher channel edge of V signal, VO₂ layer of the annealed samples has shifted forward as compared to the virgin sample while the lower channel edge matches. From this observation one concludes that the underlying layer of VO₂ has reacted with Hf. Rump simulation disclosed that V is present through out the reacted region in varying concentrations, as well as Hf and O. Both the reacted samples show the presence of a compound phase HfVO₂. These findings tell us that Hf does react with VO₂.

Al-VO₂

From the calculated values of the heats of reaction for all possible Al-VO₂ interactions resulting in the formation of Vanadium-Aluminum alloy and oxides of Aluminum may be obtained from **Table 5.1**. Consider the following reaction:



The calculated heat of reaction obtained from **Table 5.1** is equal to +35.6 kJ/ (mol.at). The heat of reaction is positive which indicates that the reaction is not thermodynamically favoured and will therefore not occur spontaneously. Consider again the following reaction:



The calculated heat of reaction obtained from **Table 5.1** is in this case equal to -68.3 kJ/ (mol.at). The heat of reaction is negative which indicates that the reaction is thermodynamically favoured and will therefore occur spontaneously.

Ta-VO₂

The calculated heat of reaction for possible Ta-VO₂ interaction are summarised in **Table 5.1** The heat of reaction was found to be negative for possible Ta-VO₂ interaction, which tells us that the reaction between Ta and VO₂ is thermodynamically favoured and can therefore proceed to occur on its own.

No experiments were done to confirm this theoretical prediction since the heat of reaction is negative for the formation of the products. No scientific findings were reported on this Ta-VO₂ system work to reveal this theoretical prediction, so therefore this remains the future work.

Rh-VO₂

The calculated values of the heats of reaction for all possible Rh-VO₂ interactions resulting in the formation of Vanadium-Rhenium alloys and oxides of Rh may be obtained from **Table 5.1**. The heat of reaction was found to be positive for all possible Rh-VO₂ interactions, which tells that the reaction between Rh and VO₂ is not thermodynamically favoured and can therefore not occur on its own.

No experiments were conducted to prove these theoretical predictions since the heats of reaction are positive for the formation of the products. No scientific findings were reported on these Rh-VO₂ systems work to prove the theoretical predictions. This remains the future work.

Zn-VO₂

Calculated values of the heats of reaction for all possible Zn-VO₂ interactions resulting in the formation of Vanadium-Zinc alloy and oxides of Zn may be obtained from **Table 5.1**. The heat of reaction was found to be negative for all possible Zn-VO₂ interactions, which indicates that the reaction between Zn and VO₂ is thermodynamically favoured and therefore will occur on its own.

No experiments were conducted to prove these theoretical predictions since the heats of reaction are negative for the formation of the products. No scientific findings were reported on these Zn-VO₂ systems work to prove the theoretical predictions. This remains the future work.

Sn-VO₂

Calculated heats of reaction for all possible Sn-VO₂ interactions are summarised in **Table 5.1**. The heat of reaction was found to be positive for all possible Sn-VO₂ interactions, which tells us that the reaction between Sn and VO₂ is not thermodynamically favoured and can therefore not occur on its own.

5.5 Correlation with electronegativity

Values of electronegativity of the metals may also be used to predict whether a metal will react with VO₂ or not [21]. R. Pretorius *et al.*[21] calculated electronegativity as an average of three electronegativities and based it on the Pauling scale. The three electronegativities used are the Allred-Rochow, Pauling and relative compactness electronegativities. The average electronegativity used in this work is based on the Pauling scale, which is the widely used scale for the given metals and their values are arranged in ascending order. The third column gives the heats of reaction range in kJ/(mol.at), which was calculated for each metal-VO₂ reaction. It can be seen from **Table 5.3** that of all the metals that react with VO₂, Co has the lowest value of electronegativity which is 1.66 for those metals which do not react with VO₂. From this observation one would expect all those metals whose electronegativity values are less than 1.66 to react with VO₂ and those with electronegativity greater than or equal to 1.66 do not react with VO₂. Al has an electronegativity of 1.77 and therefore is expected not to react if one considers only its average electronegativity, however the calculated heat of reaction for Al is negative and this suggests that it does react with VO₂. Experimental results show that it does react with VO₂.

Fig. 4.5.1 is a plot of average electronegativity (Pauling scale) versus heats of reaction (ΔH_R) in kJ/ (mol.at) for various metals interacting with VO₂, for all cases where data could be obtained. Crosses refer to elements listed at the top of the graph and circles refer to those elements listed at

the bottom. No reaction is expected for elements with positive heats of reaction whereas for elements where all heats of reaction are negative, a reaction is expected.

TABLE 5.3: *Metal-VO₂ interaction results compared with calculated heats of reaction and average electronegativity of the metal.*

Metal	Average electronegativity Pauling scale	Heats of reaction Range (ΔH_R) kJ/ (mol.at)	Chemical reaction?
Hf	1.17	-96.85	Yes
Ta	1.29	-24.9	Yes
Co	1.66	+22.6 to 50.5	No
Ni	1.67	+12.2 to + 78.3	No
Pt	1.67	+50.4 to +119.5	No
Pd	1.71	+51.4 to +174.4	No
Al	1.77	-83.56 to + 121.8	Yes
Rh	1.94	+41.1 to 270.99	No
Zn	2.10	-2.66 to -0.998	Yes

To find a point of electronegativity above which metals do not react with VO_2 and below which they do react, a plot shown in **Fig. 4.5.1** was constructed. **Fig. 4.5.2** shows a plot of the most negative heats of reaction for each metal versus the average electronegativity (Pauling scale). A straight line drawn through the points crosses the zero value of heat of reaction at about 1.70 indicating that those metals with electronegativity less than 1.70 should react with VO_2 . From **Table 5.3** it is seen that Palladium (Pd) has an average electronegativity of 1.71, which is more than the value of the cross point, which is 1.70. Pd is therefore not expected to react with VO_2 .

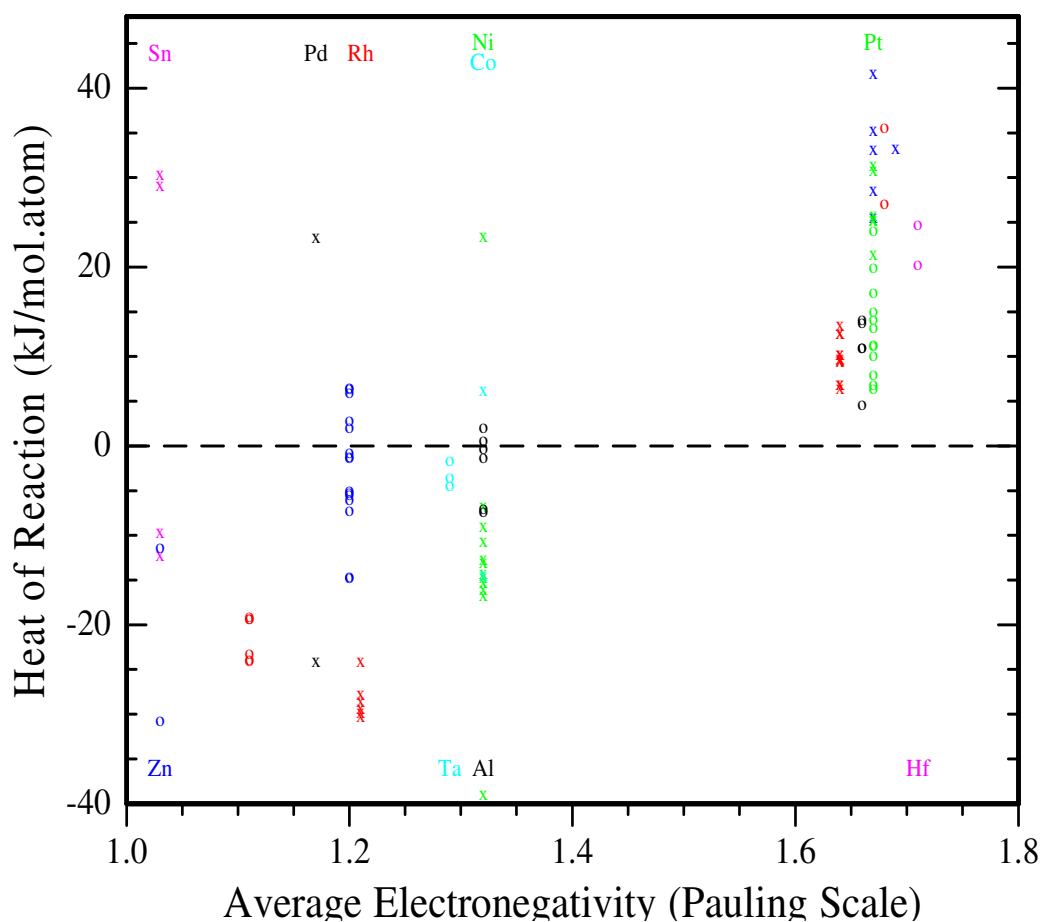


FIGURE 5.5.1: *Heats of reaction for metals. Heats of reaction are plotted on the vertical axis versus electronegativities on the horizontal axis.*

Experimental results obtained for Pd were found to be in agreement with this conclusion. They showed that Pd does not react with VO_2 . Al is rather a strange case. It has an average electronegativity of 1.77 which is more than 1.70 therefore one would expect it not to react with VO_2 , but the calculated heat of reaction for Al is negative which means that it does react with VO_2 . Zn, has a negative heat of reaction which tells us that it does react with VO_2 . Experimental evaluation for Al results showed that Al is unstable when in contact with VO_2 , it therefore does react with VO_2 to form some of its phases.

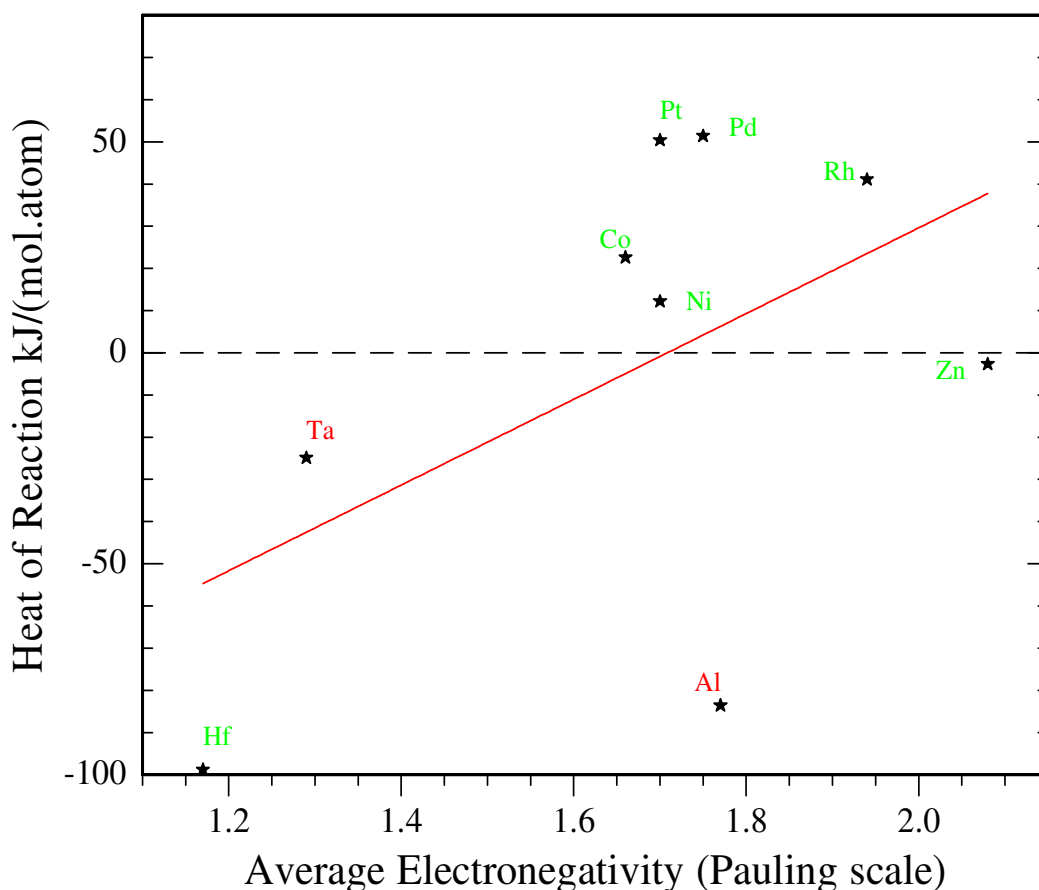


FIGURE 5.5.2: Average electronegativity has been plotted against the most negative values of the heats of reaction in kJ/(mol.at). The best fitting straight line through the points was obtained. The straight line intercepts the electronegativity axis at a value of 1.70. Metals whose electronegativity are less than 1.70 are expected to react with VO_2 .

Electronegativity parameter ϕ^* of the Miedema model [20] can also be used in a similar manner as the average electronegativity to predict interaction between metals and VO₂.

Table 5.4 shows electronegativity values in Volts for the given metals. These values are arranged in ascending order. Column three gives the range of heats of reaction in kJ/(mol.at), which were calculated for each possible metal reaction with VO₂. **Fig. 4.5.3** is a plot of the electronegativity parameter ϕ^* (in Volts) of the Miedema [19] model versus calculated heats of reaction (ΔH_R) in kJ/(mol.at) (see **Table 5.2**) for various metals interacting with VO₂. Crosses refer to elements listed at the top of the graph and circle refers to those elements listed at the bottom. In **Fig. 4.5.3** all metals having negative ΔH_R values are expected to react with VO₂ while those with positive ΔH_R values are not expected to react with VO₂. To find the cross over point i.e. the value of volts parameter above which metals do not react with VO₂ and below which they do react, a plot in **Fig. 4.5.4** was constructed. **Fig.4.5.4** shows a plot of the most negative heat of reaction for each metal versus the electronegativity parameter ϕ^* . A straight line drawn through the points crosses the zero value of heat of reaction at about 4.67 V indicating that those metals with electronegativity equal to or less than 4.67 V should react with VO₂.

TABLE 5.4: Metal-VO₂ interaction results compared with calculated heats of reaction and the electronegativity parameter ϕ^* as defined by Miedema [10, 13, 19, 25].

Metal	Average electronegativity Pauling scale	Heats of reaction Range (ΔH_R) kJ/(mol.at)	Chemical reaction ?
Hf	3.60	-96.85	Yes
Ta	4.05	-24.9	Yes
Zn	4.10	-2.66 to -0.998	Yes

Cont...

Metal	Average electronegativity Pauling scale	Heats of reaction Range (ΔH_R) kJ/(mol.at)	Chemical reaction ?
Al	4.20	-83.56 to + 121.8	Yes
Co	5.10	+22.3 to 50.5	No
Ni	5.20	+12.2 to + 78.3	No
Rh	5.40	+41.1 to 270.99	No
Pd	5.45	+51.4 to +174.4	No
Pt	5.65	+50.4 to +119.5	No

It can be observed from **Table 5.4** that the value of ϕ^* for Al is 4.20 V. From this observation Al is expected to react with VO₂, our experimental results show that does react with VO₂.

Sn on the other hand has a ϕ^* value of 4.15 V which is less than 4.20 V and therefore Sn according to **Table 5.4** is expected to react, our experimental results reveal that it does not react. In **Table 5.4** metals whose Miedema electronegativity values are greater than 4.67 V are Co, Ni, Rh, Pd and Pt. These metals are therefore not expected to react with VO₂, experimental results showed this to be true with the Miedema electronegativity values. Metals like Zn, Ta, Sn, Hf are among those metals whose Miedema electronegativity values are less than 4.67 and are therefore expected to react with VO₂. However, our experimental results showed that Hf react with VO₂. In the case of Zn, Ta and Sn no experiments were conducted to reveal this theoretical evaluations.

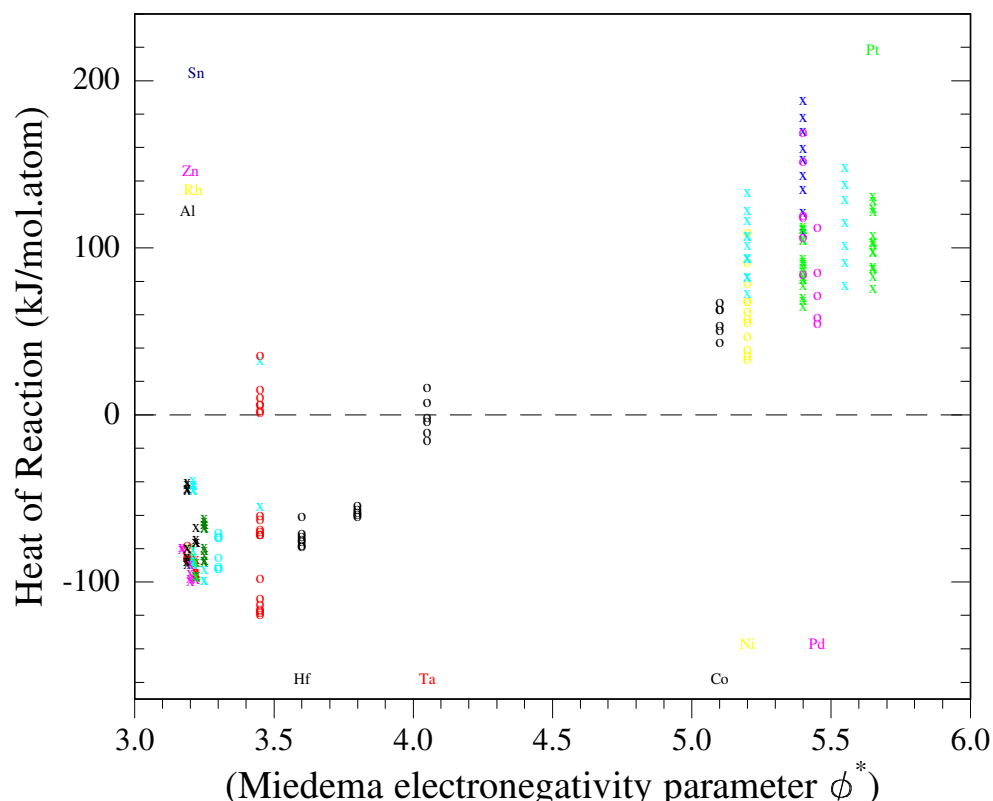


FIGURE 5.5.3: Heats of reaction of various metals when in contact with VO_2 . Heats of reaction are plotted on the vertical axis and on the horizontal is Miedema electronegativity parameter ϕ^* .

5.6 Prediction of interaction using ternary phase diagrams.

Ternary phase diagrams can be used as a tool to predict the solid state interactions in thin metal films involving binary systems. Most of the work involving the use of ternary phase diagrams for prediction of interaction was focused on refractory metal- SiO_2 systems, because of their use in integrated circuit interconnects schemes. Beyer *et al.*[22] have indicated that thermodynamic considerations may be used to draw, at any temperature, a ternary phase diagram capable of predicting thin film reactions of a three element system involving refractory metal, silicon and oxygen. The use of ternary phase diagrams for prediction of interaction is discussed in details in section 1.4.1 for the Ti-Si-O. In this section we use the same method to predict solid state interactions between metals and VO_2 .

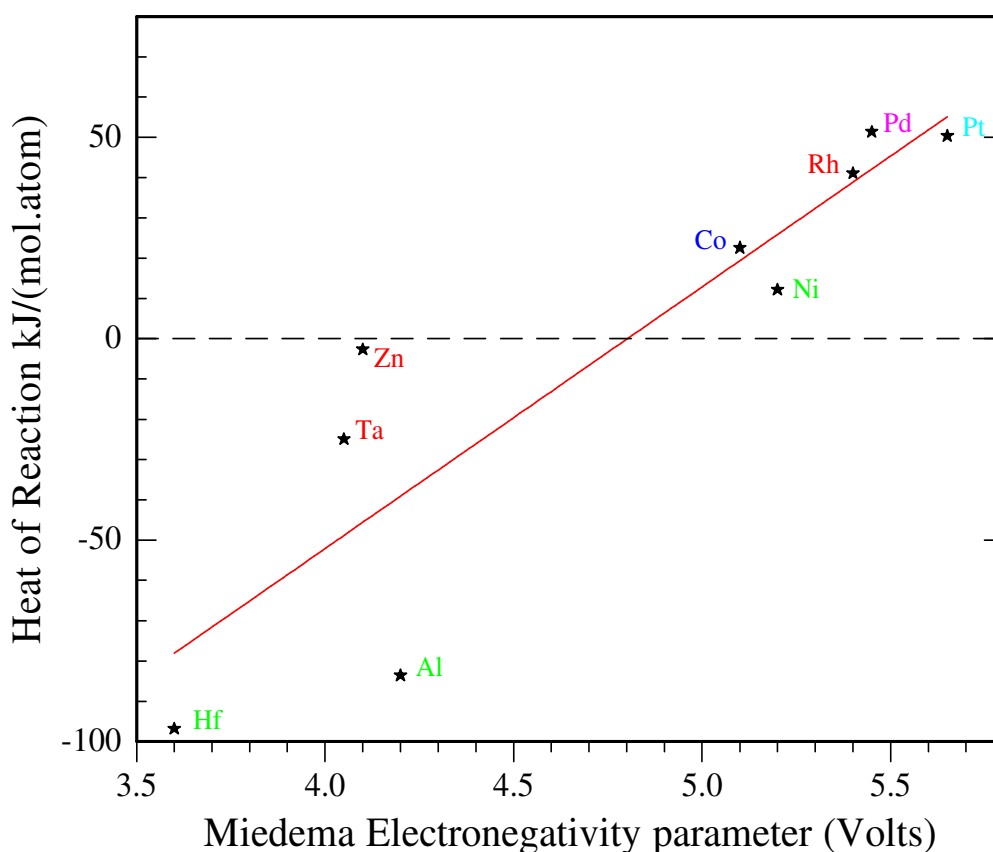


FIGURE 5.5.4: The electronegativity parameter ϕ^* has been plotted against the most negative value of the Heats of reaction in kJ/(mol.at). The best fitting straight line through the points was obtained. The straight line intercept the ϕ^* axis at a value 4.67 V. Metals whose electronegativities great than 4.67V are expected to react with VO_2 and those electronegativities are more than are expected not to react with VO_2 .

Since the experiments involve a ternary system and are done at fixed temperature and pressure, according to the Gibbs phase rule there showed be a maximum of three phases in equilibrium in any part of the phase diagram. The phase diagrams that follow are based on the method first developed by R. Beyers [23], which is explained in chapter 1. In these diagrams the solid tie lines connecting any phases mean that those phases can co-exist in equilibrium, without any chemical reaction between each other i.e. they are chemically stable when put into contact with each other.

Pd-VO₂

Fig. 4.6.1 shows a ternary phase diagram obtained for the Pd-VO₂ system. The solid line (or tie line) between Pd and VO₂ indicates that VO₂ is stable when in contact with Pd. This tie line was first obtained by calculating the heat of reaction corresponding to the point where the possible tie lines would cross (see **Table 5.6.1** below).

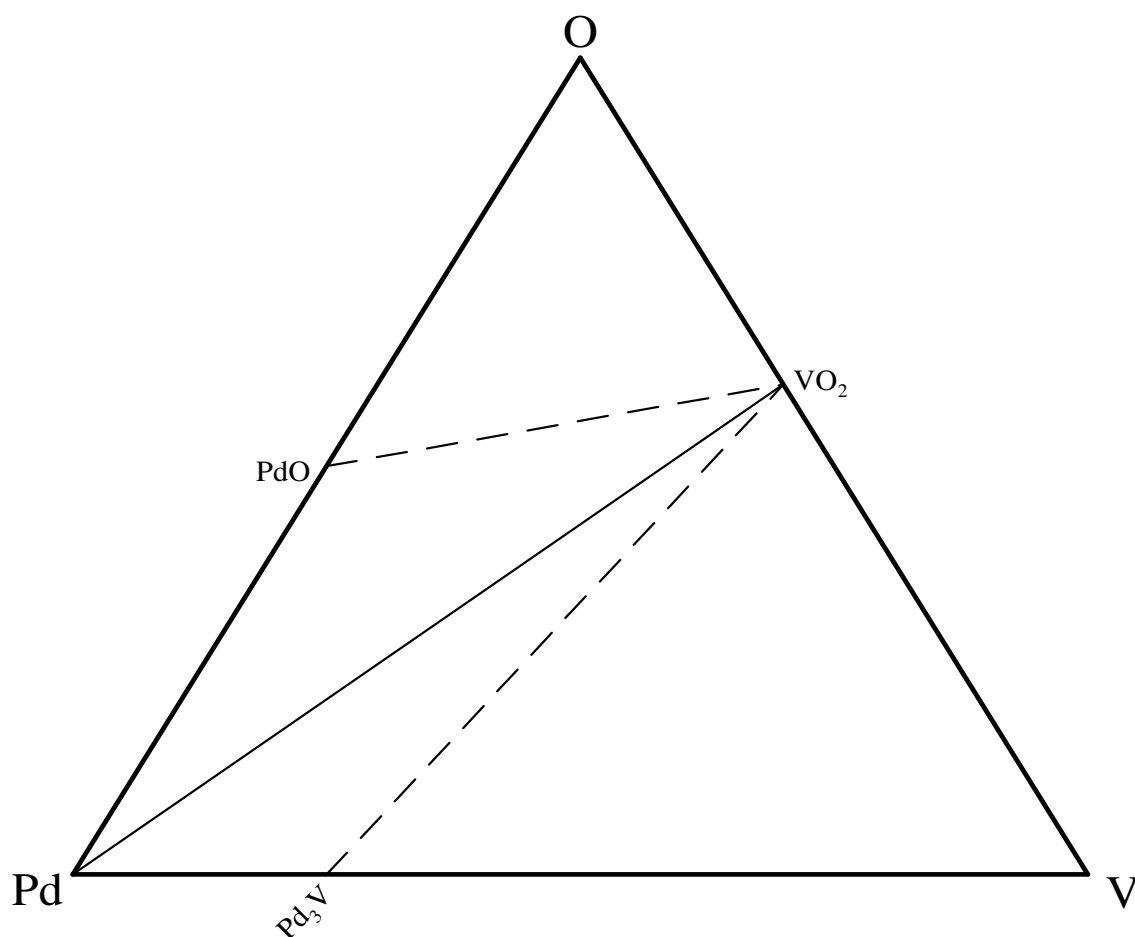


FIGURE 5.6.1: Ternary phase diagram for Pd-VO₂. The solid tie line between Pd and VO₂ indicates that VO₂ is stable when in contact with Pd. The dashed lines also indicate stability and they were obtained through thermodynamic calculations.

The negative value obtained for this reaction means that the reaction to the right is thermodynamically favoured and will therefore proceed resulting in the formation of Pd and VO₂

stable phases, thus a tie line between these phases exists meaning that VO₂ is stable when in contact with Pd.

TABLE 5.6.1: Heat of reaction calculation to investigate the presence of a tie line between VO₂ and Palladium (Pd) metal at equilibrium.

Tie line reactions	ΔH_R kJ/(mol.at)
$V + 2PdO \rightarrow 2Pd + VO_2$	-108.50

Experimental results for Pd-VO₂ samples annealed up to a temperature of 700°C confirm this i.e. VO₂ is stable when brought into contact with Pd for temperature up to 700°C. The broken lines also suggest stability and were inferred from thermodynamic calculations.

Co-VO₂

Fig. 4.6.2 shows a ternary phase diagram obtained for the Co-V-O system. The solid line also called tie line between Co and VO₂ indicates that VO₂ is stable when in contact with Co. This tie line was first obtained by calculating the heat of reaction corresponding to the point where the possible tie lines would cross (see **Table 5.6.2** below). Experimental results for Co-VO₂ samples annealed up to a temperature of 700°C confirm this i.e. VO₂ does not react with Co for temperatures up to 700°C. The negative value obtained for this reaction means that the reaction to the right is thermodynamically favored and will proceed resulting in the formation of Co and VO₂ stable phases, thus a tie line between these phases exists meaning that VO₂ is stable when in contact with Co.

TABLE 5.6.2: Heat of reaction calculation to investigate the presence of a tie line between VO_2 and Cobalt (Co) metal at equilibrium.

Tie line reactions	ΔH_R kJ/(mol.at)
$\text{V} + 2\text{CoO} \rightarrow 2\text{Co} + \text{VO}_2$	-47.08
$2\text{V} + \text{Co}_3\text{O}_4 \rightarrow 3\text{Co} + 2\text{VO}_2$	-57.97

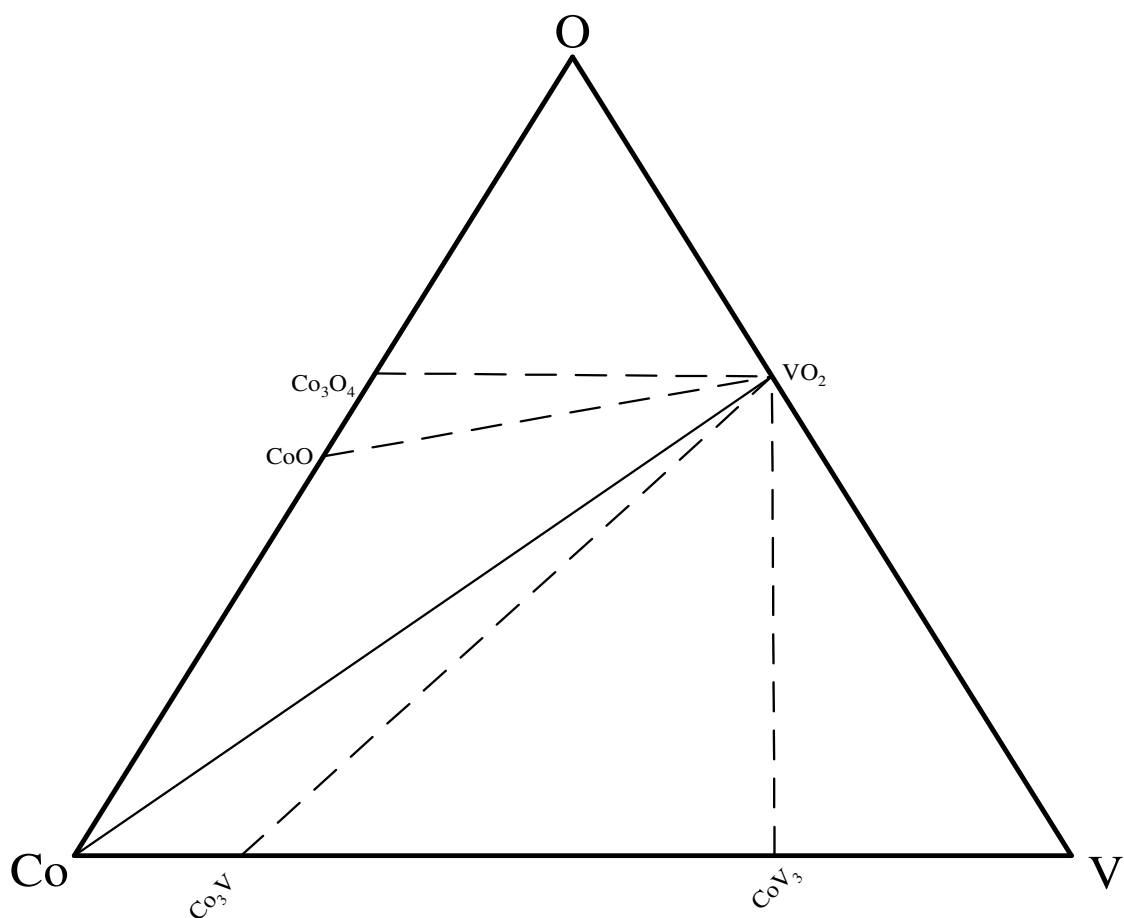


FIGURE 5.6.2: Ternary phase diagram for Co-V-O. The solid line between Co and VO_2 indicates that VO_2 is stable when in contact with Co. The broken lines also suggest stability and they were obtained through thermodynamic calculations.

Ni-VO₂

Fig. 4.6.3 Is a ternary phase diagram obtained for the Ni-VO₂ system as shown. A tie line exists between Ni and VO₂, which indicates that VO₂ is stable when brought into contact with Ni. Calculations for heat of reaction corresponding to the point where the possible tie lines would cross give a negative value for this reaction (see **Table 5.6.3**). Therefore there must be a tie line between these phases thus indicating that VO₂ is stable when in contact with Ni i.e. Ni does not react with VO₂. Our experimental results obtained for this system confirm this stability for temperature up to 700°C.

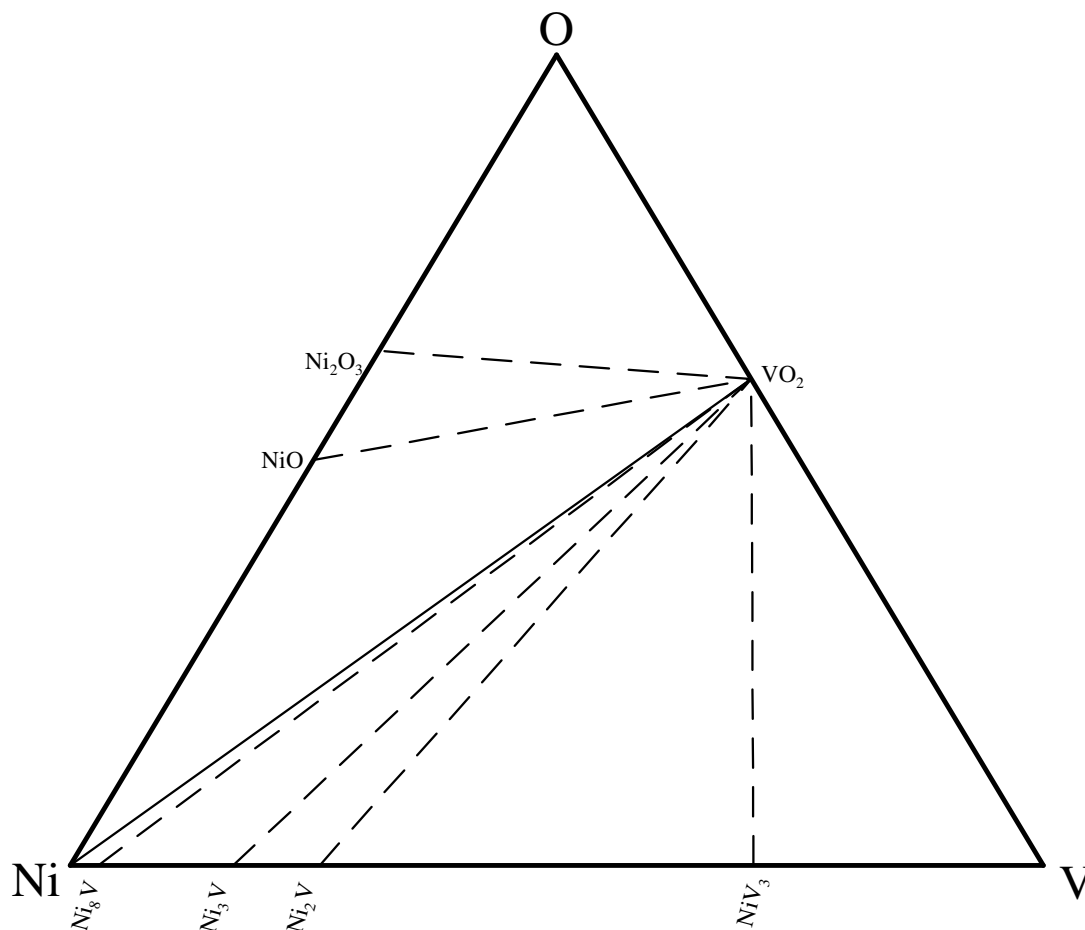


FIGURE 5.6.3: Ternary phase diagram for Ni-V-O. The solid line between Ni and VO₂ indicates that VO₂ is stable when in contact with Ni. The dashed lines also indicate stability and they were obtained from thermodynamic calculations.

TABLE 5.6.3: Heat of reaction calculation to investigate the presence of a tie line between VO₂ and Nickel (Ni) metal at equilibrium.

Tie line reactions	ΔH_R kJ/(mol.at)
$V + 2NiO \rightarrow 2Ni + VO_2$	-46.44
$3V + 2Ni_2O_3 \rightarrow 4Ni + 3VO_2$	-89.30

Pt-VO₂

Fig. 4.6.4 Is a ternary phase diagram obtained for Pt-VO₂ system. The tie line between VO₂ and Pt means that VO₂ is stable when in contact with Pt. Calculations for heat of reaction corresponding to the point where the tie line would cross give a negative value for this reaction (see **Table 5.6.4**), thus there is a tie line between Pt and VO₂ and therefore the two do not react. Our experimental results confirm this stability up to 700°C temperature.

TABLE 5.6.4: Heat of reaction calculation to investigate the presence of a tie line between VO₂ and Platinum (Pt) metal at equilibrium.

Tie line reactions	ΔH_R kJ/(mol.at)
$V + 2PtO \rightarrow 2Pt + VO_2$	-114.20
$2V + Pt_3O_4 \rightarrow 3Pt + 2VO_2$	-140.40
$V + PtO_2 \rightarrow Pt + 3VO_2$	-144.75

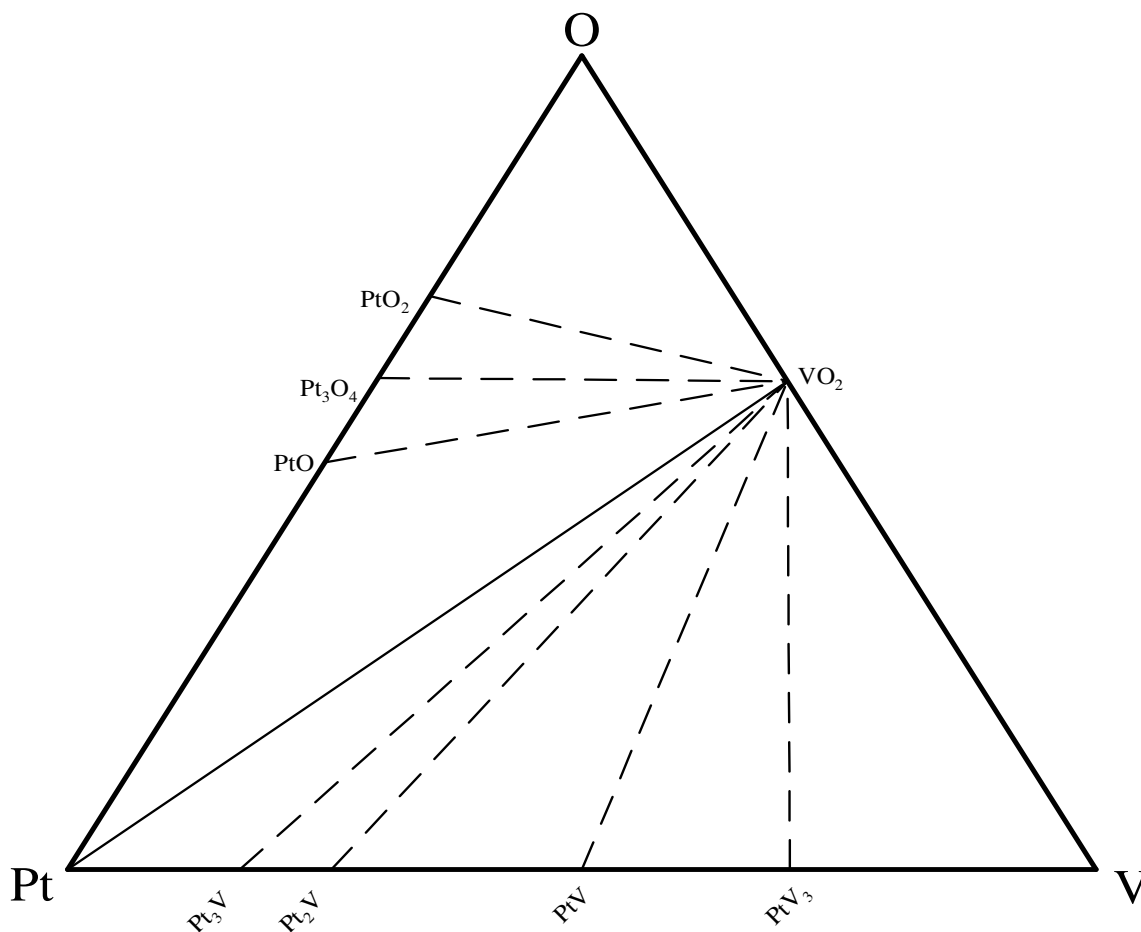


FIGURE 5.6.4: Ternary phase diagram for Pt-V-O. The solid line (tie line) between Pt and VO_2 indicates that VO_2 is stable when in contact with Pt. The dashed lines also suggest stability and they were obtained through thermodynamic calculations.

Rh- VO_2

Fig. 4.6.5 shows a ternary phase diagram obtained for the Rh-V-O system. The tie line between Rh- VO_2 was obtained by calculating the heat of reaction corresponding to the point where the tie lines would cross (see **Table 5.6.5**). The negative value obtained for this reaction means that the reaction to the right is thermodynamically favoured and will therefore proceed resulting in the formation of Rh and VO_2 stable phases, thus a tie line between these phases exists meaning that VO_2 is stable when in contact with Rh.

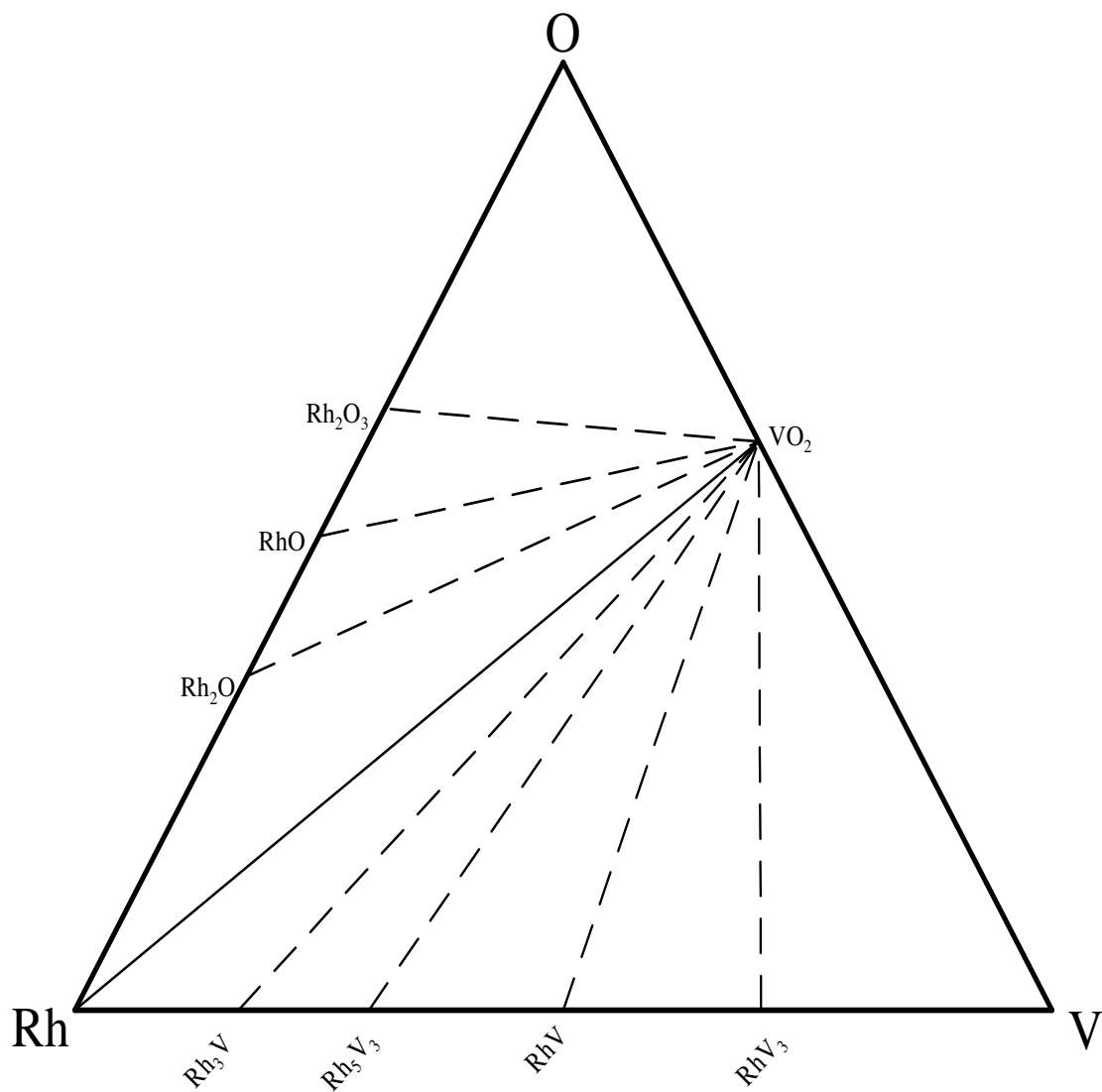


FIGURE 5.6.5: Ternary phase diagram for Rh-V-O. The solid line (tie line) between Rh and VO₂ indicates that VO₂ is stable when in contact with Rh. The dashed line also indicates stability and they were obtained through thermodynamic calculations.

Sn-VO₂

Fig. 4.6.6 shows a ternary phase diagram obtained for the Sn-VO₂ system. A tie line exists between Sn and VO₂, which tells that Sn is stable when in contact with VO₂. Calculations for the heat of reaction corresponding to the point where the possible tie line would cross give a negative value for this reaction (see **Table 5.6.6**). Therefore there must be a tie line between these phases thus indicating that VO₂ and Sn are stable when brought together i.e. VO₂ does not react with Sn.

TABLE 5.6.5: Heat of reaction calculation to investigate the presence of a tie line between VO₂ and Rhenium (Rh) metal at equilibrium.

Tie line reactions	ΔH_R kJ/(mol.at)
$V + 2Rh_2O \rightarrow 4 Rh + VO_2$	-74.66
$V + 2RhO \rightarrow 2Rh + VO_2$	-106.52
$3V + 2Rh_2O_3 \rightarrow 4Rh + 3VO_2$	-159.55

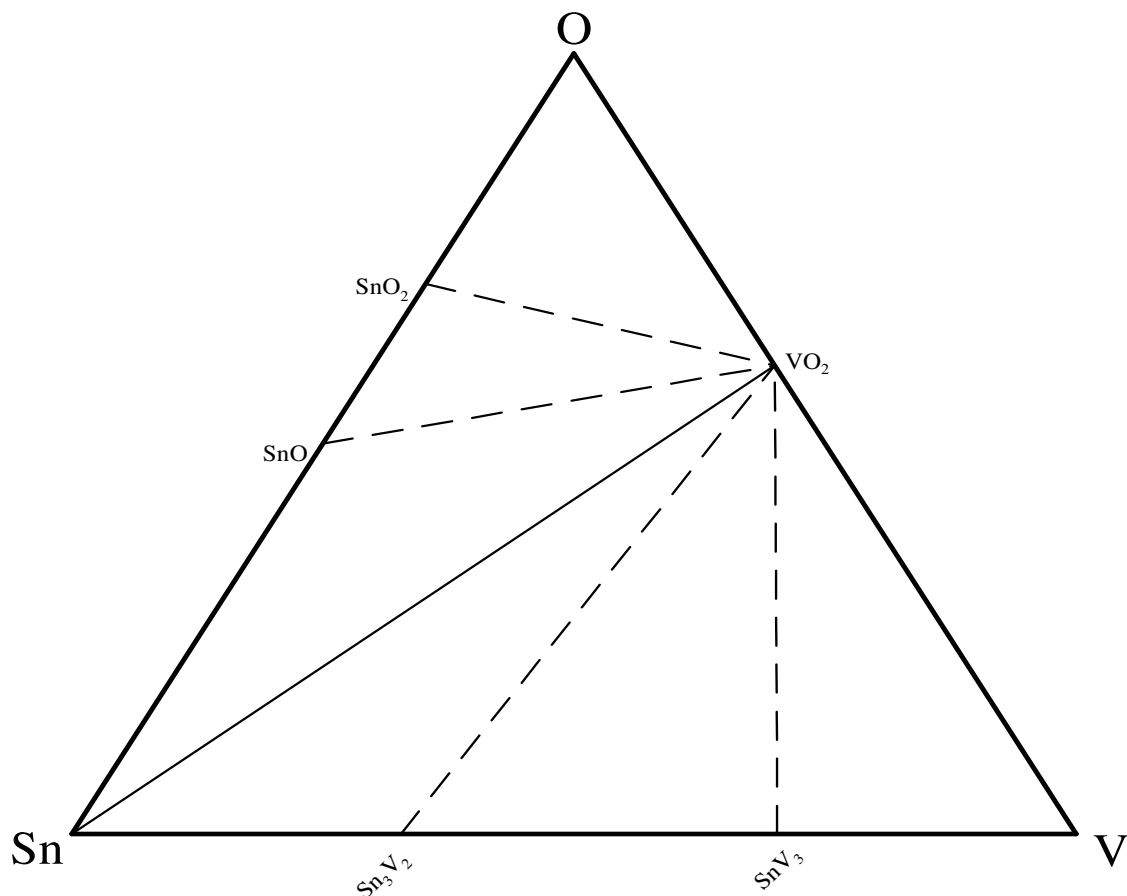


FIGURE 5.6.6: Ternary phase diagram for Sn-V-O. The solid line (tie line) between Sn and VO₂ suggests that VO₂ is stable when in contact with Sn. The dashed lines also suggest stability and they were obtained through thermodynamic calculations.

TABLE 5.6.6: Heat of reaction calculation to investigate the presence of a tie line between VO₂ and Tin (Sn) metal at equilibrium.

Tie line reactions	ΔH_R kJ/(mol.at)
$V + SnO_2 \rightarrow Sn + VO_2$	-323.55
$V + 2SnO \rightarrow 2Sn + VO_2$	-30.36

Al-VO₂

Fig. 4.6.7 shows a ternary phase diagram obtained for the Al-VO₂ system. The solid line (or tie line) between Al and VO₂ indicates that VO₂ is stable when in contact with Al. This tie line was obtained by calculating the heat of reaction corresponding to the point where the possible tie line would cross (see **Table 5.6.7**). The negative value obtained for this reaction means that the reaction to the right is thermodynamically favoured and will therefore proceed resulting in the formation of Al and VO₂ stable phases, thus a tie line between these phases exists meaning that VO₂ is stable when in contact with Al. In the case of Al a positive value was obtained meaning that an Al oxide is stable and will form VO₂ and Al as products. Experimental results for Al-VO₂ samples annealed up to 700°C showed that Al does react with VO₂ forming some of its phases. The dashed lines also indicating stability and were inferred from thermodynamically calculations.

TABLE 5.6.7: Heat of reaction calculation to investigate the presence of a tie line between VO₂ and Aluminum (Al) metal at equilibrium.

Tie line reactions	ΔH_R kJ/(mol.at)
$V + 2Al_2O \rightarrow 4Al + VO_2$	-64.77
$V + 2AlO \rightarrow 2Al + VO_2$	-179.16
$3V + 2Al_2O_3 \rightarrow 4Al + 3VO_2$	+93.17

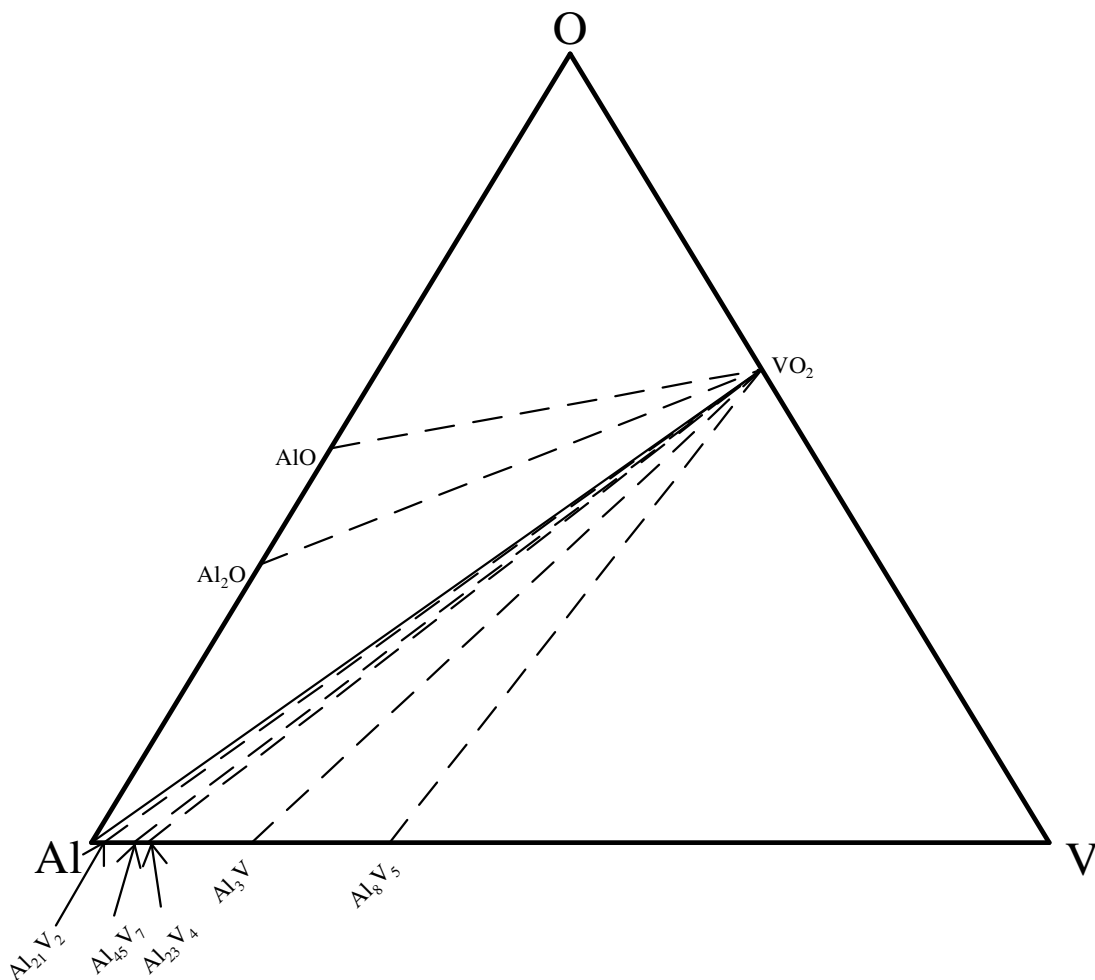


FIGURE 5.6.7: Ternary phase diagram for Al-V-O. The solid line (tie line) between VO_2 and Al indicates that VO_2 is stable when in contact with Al. The broken lines also suggest stability and were obtained through thermodynamic calculations.

5.7 Conclusion

A condition for thermodynamic stability of VO_2 -metal thin films was conducted. Various models were used to predict the reaction between the metals and VO_2 . The metals which were brought in contact with VO_2 are Pt, Co, Ni, Pd, Hf, and Al. Thermodynamics models which is based on the Gibb's free energy demonstrate to be a useful tool to predict whether a metal will react with VO_2 or not. The electronegativity was also used to predict whether a reaction is possible or not. Our experimental results agree with Miedema and the average electronegativity prediction parameters were used as well.

Ternary phase diagrams can be used as an aid in predicting results between metal/ VO_2 interactions. The ternary phase diagrams have been drawn based on the heats of reaction that are positive to check if their products are unstable (i.e $\text{V} + \text{metal Oxide} \rightarrow \text{metal} + \text{VO}_2$). These phase diagrams tell us that metal and VO_2 are stable and will therefore not form any phase. These ternary phase diagrams have been developed and they do correlate with our experimental results. The ternary phase diagrams for the systems used showed to be in agreement with our experimental results.

CHAPTER 6

SUMMARY AND CONCLUSION.

6.1 Introduction

Materials displaying the remarkable combination of high electrical conductivity and optical transparency already from the basis of many technological applications including optical thin films and interference coatings, solar energy capture and other opto-electronic devices [30]. Here we present the fabrication and the basic investigation on the interaction of these material/s oxides in contact with other metals, whether will produce other materials. Metal-nonmetal transition in many transition-metal oxides has been the subject of interest [7]. In this work specifically the thermodynamic stability of metal oxide VO_2 was investigated its interaction with various metals. The aim is to fully understand the basic performance and to set for new or improved materials which will breach the limits for new-generation transparent conducting materials, either oxides or beyond oxides, simply because when VO_2 react with a metal some products may be formed which are the ones that can add new application and for general scientific knowledge.

We investigated the interaction of VO_2 when in contact with other metals. The purpose was on synthesizing, checking if correct material to investigate was found, and detecting, identifying the reaction took place to form products or compound phases at the interface. The method used to confirm pure phase of VO_2 is UV-VIS-NIR spectrometry and X-Ray Diffraction. The identification methods used after making of samples were done were Rutherford Backscattering

Spectrometry (RBS) and X-Ray Diffraction (XRD) in case there was a compound phase observed. A theoretical evaluation was done and compared to our experimental results obtained. The aim was to see if there will be a reaction or not as in the case of theoretical predictions suggest. Heats of reaction were used; average electronegativities [21], the Miedema model electronegativities as well as ternary phase diagrams developed by Beyer [22].

6.2 Summary

The metals investigated in this work are Pd, Ni, Hf, Pt, Ta, Co, Rh, Al, Zn, and Sn. We investigated interactions of vanadium dioxide with metals. It was difficult to synthesis Vanadium dioxide (VO_2) since this material belongs to a phase diagram that has many V-O phases which is shown in **chapter 2**. One has to make sure that the correct and proper optimised conditions are achieved that give the pure VO_2 phase before proceeding with the experiments involving deposition of metal on the VO_2 film. The experimental results obtained for synthesis of VO_2 are displayed and discussed in **chapter 3**. The pure phase of VO_2 was synthesized using the magnetron rf reactive sputtering under the correct optimise conditions. The film was deposited on a corning glass as a substrate at a temperature of 450°C for 2 hours. The film was taken for characterization to check if pure VO_2 phase is achieved and those conditions that showed to be reliable were kept the same when making the other samples. **Fig. 2.4** and **Fig. 2.5** show the measured optical properties of VO_2 which are found to be comparable to the theoretical properties [1-4]. Given in the literature for example VO_2 at temperature less than 68°C has a high IR transmittance and behave as an insulator with a monoclinic structure confirmed with an X-Ray Diffraction (XRD) shown in **Fig. 2.3**, whereas above this temperature it behaves as a metal and is highly reflective as shown in **Fig.2.4**. Experimental results obtained for metals are discussed in **chapter 4**. Pt thin films were made and it did not show any interaction with VO_2 . It also showed no sign of oxidation. One Pt sample was annealed at temperature of 700°C for 1 hour. The spectrum for RBS of the annealed sample did not show any interaction between VO_2 and Pt since no oxidation was observed. The RBS spectrum of the annealed sample matches with the as-deposited sample and this signified that Pt does not react with VO_2 even at higher annealing temperature of 700°C for 1 hour. The calculated values of heats of reaction for Pt and VO_2 were found to be positive for all the compound phases which suggested that the reaction

between VO_2 and Pt is not thermodynamically favoured and will not proceed to form any products. This is in agreement with our experimental results. The average electronegativity value for Pt was calculated to be 1.70. The cross over point was 1.70 and metals below or less than this value may react with VO_2 and those greater than this value may not react. Pt is on a cross over point is therefore not expected to react. These values were on the Pauling scale for heats of reaction against the average electronegativities for all metals investigated. Considering also Miedema electronegativity Pt has a value of 5.65 V and the cross over point is 4.67 V, therefore according to Miedema electronegativity Pt was not expected to react and our experimental findings confirmed that Pt does not react with VO_2 to form product and are therefore thermodynamically stable to each other. These values were plotted as heats of reaction against Miedema electronegativity as Volts. Metal whose values are less than 4.67 V are expected to react while those whose values above 4.67 V are expected not to react. The ternary phase diagram of stability which involves Pt, V, and O as shown in **Fig. 4.6.4** has a solid line between Pt and VO_2 indicating Pt is stable when in contact with VO_2 was up to a temperature of 700°C .

Thin film interaction of Pd deposited on VO_2/glass was investigated. Two samples of structure $\text{Pd}(2070\text{\AA})/\text{VO}_2(6000\text{\AA})/\text{glass}$ with one sample kept under vacuum to avoid oxidation was treated as a virgin sample, the other sample was annealed at temperatures up to 700°C for 1 hour. RBS results for virgin spectrum showed no interaction between Pd and VO_2 and no sign of oxidation was seen. The spectrum of sample annealed was then compared to that of the virgin sample and the two spectra matched. This tells us that there were no reactions between Pd and VO_2 for the annealing temperature of 700°C for 1 hour. The values of heats of reaction of Pd and VO_2 were calculated and found to be positive for all compound phases. This suggested that there is no reaction between Pd and VO_2 even at higher annealing temperature of 700°C for an hour. VO_2 is thermodynamically stable when in contact with Pd at temperature of 700°C for 1 hour. Considering the average electronegativity of Pd, it has a value of 1.71 which according the cross over point of 1.70 metals with electronegativity less than this value will react while those with electronegativity above this value are expected not to react with VO_2 , Pd is not expected to react with VO_2 hence our experimental results showed it to be true. Then checking the Miedema electronegativity ϕ^* which has a cross over point of $\phi^* = 4.67$ V. Pd has a ϕ^* of 5.45 and one could see that Pd will not react with VO_2 and thus our experimental observation show that it does not react. The ternary phase diagram of stability for Pd, V, and O as in Fig. 4.6.1 has a solid line

between Pd and VO₂ which suggests that Pd is stable when in contact with VO₂ and that was confirmed with our experimental results. Results obtained for Hf showed that Hf reacts with VO₂. Looking at the RBS results for the as-deposited sample it shows no interaction between Hf and VO₂. There were three samples in this investigation; one was treated as a virgin, while the other two samples were annealed at two different temperatures for the same time. One sample was annealed at 400°C for 45 minutes and the other was annealed at 450°C for 45 minutes as well. The two spectra of the annealed samples do not match with the virgin sample which shows that Hf does react with VO₂ to form compound phases which were confirmed using the X-Ray Diffraction (XRD). For the as-deposited sample on the XRD a Hf peak was observed which shows that Hf crystallizes on deposition. For sample annealed at 400°C a little peak of HfV₂ was observed which tells that a phase is forming at the interface and to sample annealed at 450°C some metal oxides of HfO₂ were also observed with HfV₂ peak growing to a strong peak.

The calculated heat of reaction for this system was found to be negative which shows that Hf is thermodynamically unstable with VO₂ and will therefore react with it to form compound phases. The electronegativity value for Hf was recorded as 1.70 on Pauling scale and the cross over point was 1.70. It is known that metal whose electronegativity is less than 1.17 and whose cross over point is less than 1.70 will react with VO₂ and those with values greater will not react with VO₂. This was confirmed with our experimental observation that Hf does react with VO₂. Again if we look at the Miedema electronegativity ϕ^* Hf has a value of 3.60 V and the cross over point is 4.67 V and Hf is expected to react with VO₂ and it does react according to our experimental results.

The ternary phase diagram of stability is not available in this work since Hf is unstable when in contact with VO₂ confirmed with our experimental results. Two samples were made on Co with one treated as a virgin sample while the other sample was annealed. The RBS spectrum for the as-deposited shows no interaction between Co and VO₂ and no sign of oxidation was observed. In the instance of the annealed sample, annealed at temperature up to 700°C for 1 hour, the RBS spectrum shows that there was no reaction between Co and VO₂ at this temperature. It does match the as-deposited spectrum, but it shows mismatch at some points, the reason for such behaviour Co peels when in contact with VO₂ after high temperature of annealing (see **Fig.4.4.3**). The values of heats of reaction for Co and VO₂ compound phase were found to be

positive which signals that there is no reaction between Co and VO₂ and this was confirmed by our experimental observation. Therefore one concludes that Co is thermodynamically stable when in contact with VO₂ at temperature up to 700°C. Co has the lower value of electronegativity which is 1.66. From this one would expect all these metals whose electronegativity values less than the cross over point of 1.70 on a Pauling scale to react with VO₂ and those with electronegativity greater than 1.70 will not react. Co has a strange case. Looking at the Miedema electronegativity ϕ^* Co has a value of 5.10 V, the cross over point has a value of 4.67 V and Co is expected not to react because its value is great than that cross over point of 4.67 V. Experimental findings correlate well with this model. Again on ternary phase diagram of stability side which involve Co, V, and O as in **Fig.4.6.2** has a solid line between Co and VO₂ indicating that Co is stable when in contact with VO₂. In the case of Ni, RBS results obtained for the two samples made with one annealed at temperature of 700°C for 1 hour, and the other one used as a virgin sample. The sample annealed at 700°C for 1 hour did not show interaction between Ni and VO₂. The RBS spectrum for the virgin sample showed no interaction. The two spectra were matching except a mismatch at V signal and at the lower energy of Ni signal which was the sign that Ni was peeling also as shown Co, Ni and Co are sometimes treated as belonging to same group with similar behaviour. Hence Ni is thermodynamically stable when in contact with VO₂ at a temperature of 700°C for 1 hour. For the heats of reaction were calculated and found to be positive for all the possible compound phases, suggesting that Ni and VO₂ are not expected to react. From our experimental observations these were confirmed at higher temperature (i.e. 700°C). Considering its average electronegativity Ni was found to be a value of 1.67. The cross over point was 1.70. The Miedema electronegativity value cross over point was found to be 4.67 V while that of Ni was 5.20 V. Thus from the electronegativity side Ni is not expected to react with VO₂.

The ternary phase diagram of stability for Ni, V, and O there was a solid line between Ni and VO₂ indicating that Ni is stable when brought together even at annealing temperature (i.e. 700°C) (see **Fig.4.6.3**) for its ternary phase diagram. Al thin films were deposited on a structure of VO₂/glass. There were two samples in this particular case. One was a virgin sample with heat treatment while the other was annealed at 530°C for 2 hours. The RBS spectrum for the as-deposited sample showed no interaction between Al and VO₂. The annealed sample showed a

reaction when compared to the as-deposited one, its height was reduced as well in V signal side suggesting that there is a reaction with Al, V, and O at the interface. The heats of reaction values for this particular case were mixed with positive and negative values showing that some of the phases will not form at the interface. What was observed is that only when Al and VO₂ produce Al₂O₃ as one of its products then Vanadium-Aluminium alloy will form and Al₂O₃ as their products. The electronegativity value for Al was 1.77 and the cross over point was 1.70 in Pauling scale, therefore Al is expected not to react with VO₂. Looking at the Miedema electronegativity value of 4.67 V as a cross over point and Al has a value of 4.20 V and is therefore expected to react with VO₂. According to our experimental observation we conclude that Al reacts with VO₂. The ternary phase diagram of stability was also constructed and there was not even a dotted line for Al₂O₃ and VO₂ because these are unstable when in contact with each other but the physics and the mechanism was not fully understood on this system.

6.3 Conclusion

A thermodynamic stability between VO₂ and metal thin films was conducted as reactions of solids brought in contact with each other and annealed at higher temperatures. A transparent conducting oxide (TCO) Vanadium dioxide was synthesized as a thin film using rf magnetron sputtering which proves to be a promising technique for VO₂ deposition. The VO₂ layer was sputtered on a Corning glass and the optical properties were investigated and showed to be comparable with the theoretical known ones. Therefore a pure VO₂ film was successfully synthesized on a Corning glass. An electron-beam was used to deposit the metal on the structure VO₂/glass in a high vacuum chamber of better than $\times 10^{-6}$ mbar. All the metals investigated were deposited on the same structure of VO₂/glass using the electron-beam evaporator. Different samples were kept as the virgin samples while other samples were annealed in a tube furnace for different time and temperature to study the interaction between the materials. All the annealing was carried out under the vacuum better than 10^{-7} kPa. All the samples were taken to do RBS on them using 2 MeV as a beam of alpha particles with a small current of 50 nA to avoid heating up the sample and cause oxidation to the easily oxidising metals i.e. Hf and Al. The Rutherford Backscattering Spectrometry spectra of the annealed sample were compared to the as-deposited spectrum to see if a reaction occurred or not. The X-Ray Diffraction (XRD) was

used to identify the observed compound phases. Atomic Force Microscope (AFM) was also used to see the surface morphology of the synthesized VO₂ layer on a glass. VO₂ peak was observed meaning that it crystallizes upon deposition on a glass. For the samples of Hf and VO₂, the VO₂ peaks were observed to all the samples, the as-deposited sample shows only VO₂ peaks and Hf suggesting that it also crystallizes upon deposition. Some of the HfV₂ and HfO₂ peaks were also observed for the annealed samples at a temperature up to 400° to 450°C for 45 minutes. For samples where a reaction had not occurred a ternary phase diagrams of stability was constructed for metal, V, and O and there was a tie line between a metal and VO₂ showing that particular metal is stable when in contact with VO₂ at the interface. All the metals investigated were having values of heats of reaction which are summarised in **Table 5.1** using the heats of formation which were extracted from **Appendix**. There was a good agreement between our experimental results and theoretical prediction based on the heats of reaction. Positive heat of reaction suggests no possible reaction between those metals in contact with VO₂ and negative heat of reaction suggests a possible reaction between those metals with VO₂ brought together. Electronegativity model was also used in prediction of possibilities of a reaction between a metal and VO₂ and to see if it does correlate well with our experimental results. Heats of reaction were drawn against average electronegativity on a Pauling scale. A fit line was constructed with a cross over value of 1.70 and those metals whose values are less than 1.70 will react with VO₂ and those greater than or equal to 1.70 will not react. Co has a strange case because it has electronegativity on a Pauling scale of 1.66 which suggests that Co will react with VO₂ but our experimental results say it does not react at temperatures up to 700°C for 1 hour. The Miedema electronegativity was used and found it to correlate well with our experiments. The ϕ^* value was 5.10 V for Co and the cross over point was 4.67 V suggesting that all metals below this value of 4.67 V will react with VO₂ whilst those above 4.67 V will not react and Co happen to be above 4.67 V and is expected not to react. Results of all the metals studied are in good agreement with the predicted ones (see **Table 5.4**). Ternary phase diagram was also used for especially those metals that did not react with VO₂ and found to correlate well with our experimental findings. The construction of ternary phase diagram of stability must at all time correlate and comply with the Gibbs phase rule which state that “there is a maximum of three (3) phases in mutual equilibrium for an arbitrary composition”. The region of these phase equilibrium form triangles of which the corner occupy the chemically compatible phases, i.e. phase which are

thermodynamically stable in contact to each other. Line can be constructed in the triangle, a tie line that connects two phases which are in equilibrium to each other.

APPENDIX

STANDARD HEATS OF FORMATION OF METAL- VANADIUM ALLOYS AND OXIDES

Element	Vanadium Alloys	ΔH_f° kJ/(mol.at)	Reference(s)	Oxides	ΔH_f° kJ/(mol.at)	Reference(s)
Pd	Pd ₃ V Pd ₂ V PdV ₃	-32.8 -42.6 -35.1		PdO	-42.7	
Ni	Ni ₃ V Ni ₈ V Ni ₂ V NiV ₃	-18.43 -8.2 -23.4 -16.29		NiO Ni ₂ O ₃	-120.3 -97.9	
Hf	HfV ₂	-2.96		HfO ₂	-381.6	
Pt	Pt ₃ V Pt ₂ V PtV PtV ₃	-41.88 -54.56 -68.27 -45.78		PtO Pt ₃ O ₄ PtO ₂	-35.6 -23.3 -44.8	
Ta	V ₂ Ta	-1.33		Ta ₂ O ₅	-292.3	
Co	Co ₃ V CoV ₃	-14.25 -12.66		CoO Co ₃ O ₄	-118.95 -127.3	
Os	OsV	-20.9	[31-32]	OsO ₂	-98.2	[31-32]

Cont...

Element	Vanadium Alloys	ΔH_f° kJ/(mol.at)	Reference(s)	Oxides	ΔH_f° kJ/(mol.at)	Reference(s)
				OsO ₃	-47.7	
				OsO ₄	-78.7	
Rh	Rh ₃ V	-27.91		Rh ₂ O	-31.8	
Rh	Rh ₅ V ₃	-39.41		RhO	-192.5	
	RhV	-44.12		Rh ₂ O ₃	-68.6	
	RhV ₃	-28.61				
Al	Al ₃ V	-24.26		Al ₂ O	-43.33	
	Al ₂₁ V ₂	-8.42		AlO	45.6	
	Al ₄₅ V ₇	-13.04		Al ₂ O ₃	-335.14	
	Al ₂₃ V ₄	-14.31				
	Al ₈ V ₅	-35.4				
Zn	V ₄ Zn ₅	-12.81		ZnO	-175.3	
	VZn ₃	-8.24				
	VZn ₁₆	-1.95				
Sn	Sn ₃ V ₂	-16.52		SnO ₂	192.5	
	SnV ₃	-15.69		SnO		
			[31-32]			
						[31-32]

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