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X-ray photoelectron spectroscopic studies of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 films

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X-ray photoelectron spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films have been investigated. The photoelectron spectrum of a simple V_2O_5 film shows the splitting of the V 2p level in accordance with the spins. The values of binding energies corresponding to V 2p and O 1s are comparable with those reported previously. For co-evaporated V_2O_5/B_2O_3 films a chemical shift in the O 1s level has been observed which has been attributed to the changed chemical environment of oxygen as a result of the presence of boron and vanadium atoms. The values of binding energies for V $2p_{3/2}$ and O 1s corresponding to simple evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 show the presence of V_2O_4 species in the films.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful technique for investigating the electronic structure of atoms, molecules and condensed matter. One of the important applications of XPS is for surface analysis. It can be used to analyse solids, gases and liquids. A particular feature of XPS is that in addition to the chemical composition of a compound, other useful information about the chemical bonds and charge distribution can be achieved. Such information can be obtained from the so-called XPS shift of core level electron lines.

In a molecule, when atoms are brought close together, the orbitals of each atom are perturbed. Relatively inner orbitals with higher binding energies may still be treated as atomic and belonging to specified atoms within the molecule, whereas the outer orbitals combine to form the valence level system of the molecule. These orbitals play an important role in the chemical bonds formed between the atoms in a molecule and which affect the charge distribution in such a way that the original neutral atoms can be considered as charged, while the neutral molecule can still retain a net charge of zero. In this situation the individual atoms in the molecule can be regarded as spheres with different charges as a result of a certain small charge transfer from one atomic sphere to the other neighbouring atoms involved in the chemical bond. This results in the shifting of the whole system of inner levels in a specified atom by a small amount which is the same for each level. Levels belonging to different atoms in a molecule are generally shifted differently. However, by using XPS chemical shifts for individual atoms in a molecule, information about the distribution of charge or potential in a molecule can be achieved [1–4]. XPS has long been applied in catalytic research due to its surface sensitivity and provides valuable information on surface electronic structure and qualitative information about the composition qualitatively [5].

Basically two types of information can be gathered on transition metal complexes: (1) data from the ligands complexed to a series of metals, and (2) data from the metal complexed to a series of ligands [4].

Theoretically the most extensively studied oxides of vanadium are VO, VO_2 and V_2O_3. The vanadium oxide with highest oxidation state (V_2O_5) is a prototype of this series of compounds and presents very interesting properties such as catalytic activity, metal–semiconductor transitions and transitions from one oxide to another form [7]. Some authors have made XPS studies of these oxides. Colton *et al.* [4] and Kasperkiewicz *et al.* [8] reported a decrease in the binding energy related to the V $2p_{3/2}$ level for V_2O_4 as compared to that for V_2O_5. Similarly, Colton *et al.* [4] and Andersson [9] noticed a decrease in the binding energy of V $2p_{3/2}$ electrons by 1.5 and 1.7 eV on going from V_2O_5 to V_2O_3, respectively. Khawaja *et al.* [10] reported that on annealing the V_2O_5 glass, the binding energy corresponding to V 2p electrons is decreased by an amount of about 0.6 eV. Sawatzky and Post [11] also observed a systematic decrease in V 2p binding energies on going from V_2O_5 via the intermediate oxides (V_2O_4 and V_2O_3) to vanadium metal. They attributed this type of decrease in binding energy to the increase in the number of 3d and 4s electrons. On the other hand, they observed an increase in the binding energies corresponding to the O 1s level on going from V_2O_2 to V_2O_3.

The binding energy of V $2p_{3/2}$ for clean metallic vanadium measured by Groenenboon *et al.* [12] and Kasperkiewicz *et al.* [8] is approximately similar ($\approx$ 512.5 eV). Kasperkiewicz *et al.* [8] also reported that the binding energies of the V $2p_{3/2}$ levels for V_2O_5

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TABLE I The binding energies (BE) of the O 1s and V 2p core lines for V_2O_5 and vanadium metal as reported by different authors

Reference	BE O 1s (eV)	BE V $2p_{3/2}$ (eV)	BE V $2p_{1/2}$ (eV)	BE difference (O 1s − V $2p_{3/2}$) (eV)
Sawatzky and Post [11]	529.8	516.9	524.3	13.0
Fujita *et al.* [13]	530.3	517.3	519.0	13.0
	for V metal	512.4	519.9	–
Colton *et al.* [4]	531.1	516.9	524.3	13.0
Blaauw *et al.* [15]	529.9	516.8	–	31.1
Khawaja *et al.* [10]	530.7	517	524.5	13.7

and V_2O_4 were 516.4 and 516.1 eV, respectively, which were almost identical, but they noticed a broadening of the V $2p_{3/2}$ linewidth for V_2O_4 compared to that for V_2O_5 and attributed it to the decrease of the oxidation state in the former material. They also recorded the differences in the binding energies of V $2p_{1/2}$ and V $2p_{3/2}$ electrons for V_2O_5 and V_2O_4 to be 7.4 and 7.0 eV, respectively. Fujita *et al.* [13] studied the XPS spectra of V_2O_5, VO_2 and V_2O_3 powders in the binding energy range 514 to 534 eV and observed an increase in the binding energy of the O 1s state and a decrease in the binding energies corresponding to V $2p_{3/2}$ on going from V_2O_5 to V_2O_3. The authors also recorded the XPS spectra of vacuum-evaporated films and found the binding energies corresponding to O 1s and V $2p_{3/2}$ to be 530.1 and 517.1 eV, respectively. The increase in the binding energies of the V 2p level on going from vanadium metal to the vanadium oxides is due to the valency increase, i.e. the number of electrons transferred from a vanadium cation to an oxygen anion. The binding energies corresponding to O 1s, V $2p_{1/2}$ and V $2p_{3/2}$ as recorded by different authors can be seen in Table I. We have investigated the X-ray photoelectron spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films.

2. Experimental procedure

Thin film complexes of V_2O_5 and V_2O_5/B_2O_3 were deposited from analytical reagent grade materials on to pre-cleaned 7059 Corning glass substrates held at an elevated temperature of about 373 K in a Speedivac coating unit Model 19A/122, at a pressure of about 10^{-6} torr (1.33×10^{-4} Pa). The co-evaporation technique developed by Hogarth and Wright [14] was used during the preparation of thin film samples. The evaporation parameters such as composition and thickness of the complex films were monitored by means of a quartz crystal monitoring system which was calibrated for each material. The total thickness of the films was measured by multiple beam interferometry making use of Fizeau fringes of equal thickness. Thin film samples were finally cut into small sizes as required by the loading conditions of the spectrometer.

The XPS spectra were recorded by a Kratos ES 300 electron spectrometer. The source of excitation was Al*Kα* X-radiation with photon energy 1486.6 eV. Firstly a broad scan survey spectrum was recorded. After completing the composition of such a scan, narrower detailed scans of the selected peaks were recorded for a more comprehensive study of the chemical composition of the films. The C 1s line was used for the charge referencing.

3. Results and discussion

The XPS spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 films are shown in Fig. 1. The binding energies corresponding to V 2p, O 1s and B 1s levels recorded in the spectra are given in Table II. While studying the XPS spectra of V_2O_5, V_2O_4 and V_2O_3 powders, it has been observed that as the

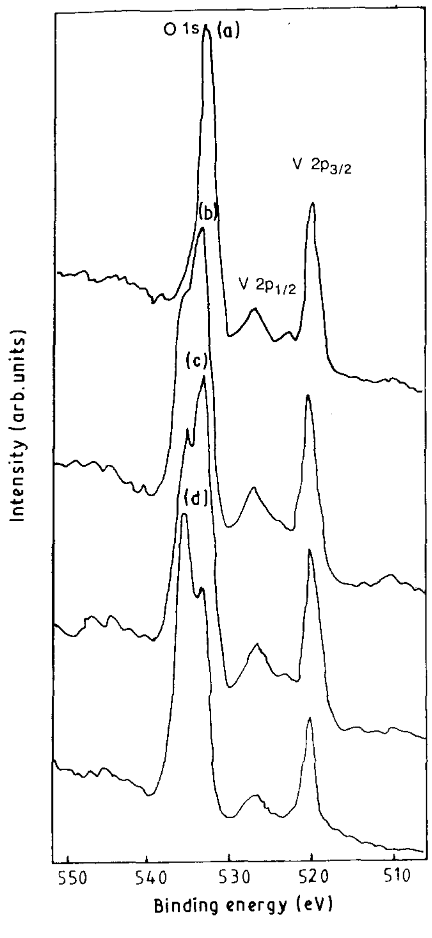


Figure 1 X-ray photoelectron spectra of V 2p and O 1s core levels for co-evaporated V_2O_5/B_2O_3 thin films of different compositions; (a) simple V_2O_5, (b) 80% V_2O_5, (c) 70% V_2O_5, (d) 60% V_2O_5.

TABLE II Binding energies of O 1s, V 2p and B 1s core levels for different compositions of co-evaporated V_2O_5/B_2O_3 thin films in the present studies

Composition	BE O 1s (eV)	BE V $2p_{3/2}$ (eV)	BE V $2p_{1/2}$ (eV)	BE difference (O 1s – V $2p_{3/2}$) (eV)	BE B 1s (eV)
100% V_2O_5	532.0	519.0	525.8	13.0	–
80% V_2O_5	532.6	519.4	526.5	13.2	197.0
70% V_2O_5	533.8	519.6	526.8	13.2	196.0
60% V_2O_5	534.0	519.8	526.8	13.2	195.8

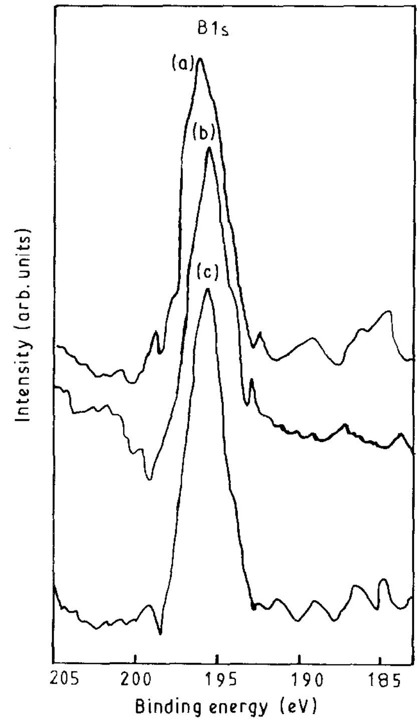


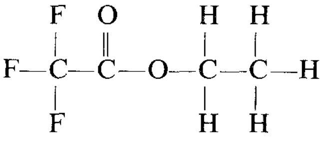
Figure 2 X-ray photoelectron spectra of B 1s core level spectra for co-evaporated V_2O_5/B_2O_3 thin films of different compositions: (a) 80% V_2O_5, (b) 70% V_2O_5, (c) 60% V_2O_5.

number of oxygen atoms combining with the vanadium atoms decreases, the binding energy of O 1s increases and that corresponding to V $2p_{3/2}$ decreases [13].

We observe that the binding energy corresponding to O 1s lies higher than those reported by different authors [4, 7, 11, 13, 15] for V_2O_5 which indicates the presence of some lower oxide species in the evaporated films. So we propose that during the evaporation process, V_2O_5 loses some oxygen, and some lower oxides of vanadium, possibly V_2O_4, are formed. The existence of such lower oxides in our samples has already been suggested by us from other observations, such as ESR, which are reported elsewhere.

It is observed that for evaporated films of simple V_2O_5, there is no splitting of the peak corresponding to O 1s. On the other hand, on increasing the content of B_2O_3 in co-evaporated V_2O_5/B_2O_3 films, splitting of the O 1s peak appears. The intensity of the split-off line which corresponds to the higher side of the binding energy and is attributed to the B_2O_3, increases with increasing content of B_2O_3.

Comparatively, relatively few XPS studies have been carried out with mixtures. Fahlman *et al.* [2] observed a similar type of splitting in the s line corresponding to sulphur in the photoelectron spectra of sodium thiosulphate. They attributed it to two different oxidation numbers (– 2 and + 6) of sulphur in the compound. Similarly, in the photoelectron spectra of a mixture of carbon monoxide and carbon dioxide gases, Siegbahn [3] observed a splitting corresponding to the O 1s line. The author related the higher energy subline of the split-off of O 1s peak to the CO and the higher energy subline to CO_2. The author also recorded the photoelectron spectrum of ethyl trifluoroacetate which has the molecular Structure I, and noted that all four carbon atoms in the molecule were distinguishable in the spectrum on the basis of different binding energies.



$$\begin{array}{ccccccccccccc} & & F & & O & & & & H & & H & & \\ & & | & & \| & & & & | & & | & & \\ F & - & C & - & C & - & O & - & C & - & C & - & H \\ & & | & & & & & & | & & | & & \\ & & F & & & & & & H & & H & & \end{array}$$

(I)

This type of behaviour can be related to the changes that occur in the core electron spectra of atoms in different chemical environments. The change in the wave-function that occurs for the outer electrons usually means a displacement of electric charge in the valence shell so that the interaction between the valence electron and the core electrons is changed. Thus a change in the chemical environment of an atom is relayed to the core electrons and induces a slight change in their binding energies, which is detectable by the X-ray photoelectron spectroscopy.

The splitting of the O 1s line in co-evaporated V_2O_5/B_2O_3 films can be explained in the following manner. The evaporated thin films contain three different elements, i.e. vanadium, boron and oxygen. Because of the different oxidation states of boron and vanadium, the oxygen atoms in the composite V_2O_5/B_2O_3 films will be effectively in two different chemical environments, and the binding energy between boron and oxygen will be different as compared to that between vanadium and oxygen. The splitting of the O 1s line in the XPS spectra of co-evaporated V_2O_5/B_2O_3 films can be attributed to such a behaviour of oxygen in the films.

For about 40% B_2O_3, the intensity of the peak corresponding to the higher energy side of the O 1s level and which is related to B_2O_3 becomes higher than that for the lower binding energy side. From these observations we conclude that when the content of B_2O_3 in co-evaporated V_2O_5/B_2O_3 films is increased beyond about 40%, the part played by B_2O_3 becomes dominant and is responsible for the relatively higher intensity of the O 1s photoelectrons corresponding to B_2O_3. This argument is further supported by the known instability of co-evaporated V_2O_5/B_2O_3 films with B_2O_3 content higher than 40% due to their hygroscopic nature, which is characteristic of B_2O_3 itself.

4. Conclusion

X-ray photoelectron spectra of co-evaporated V_2O_5/B_2O_3 films show the splitting of the V 2p level which is characteristic of transition metals. The values of binding energies corresponding to the O 1s and V 2p states suggest the existence of a lower oxide such as V_2O_4 in the films. The chemical shift of the O 1s level for co-evaporated V_2O_5/B_2O_3 films has been related to the different chemical environment for oxygen created by having both boron and vanadium in the films.

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