Vacancy-induced electronic states in substoichiometric $V_{2-x}Mo_xO_{3\pm y}$ thin films and powders—A soft X-ray emission study

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MS received 24 October 1998; revised 17 February 1999

Abstract. Vanadium oxide as well as molybdenum oxide thin films have been found to show electrochromism and metal insulator transitions. Incorporation of vanadium ion into molybdenum oxide lattice not only changes the lattice parameters but also shows prominent spectral changes in X-ray emission spectra. $K_{\beta 1-3}$ emission spectra of vanadium in different alloy films of V_2O_5 – MoO_3 system have been studied here and these have been compared with the X-ray emission spectra of similar composition of V_2O_5 – MoO_3 powders. For $K_{\beta 1-3}$ emission, the difference in values of asymmetry indices of thin films and powders is marginal, although considerable tailing towards high energy is observed in thin films. By curve fitting procedure, the $K_{\beta 1-3}$ emission spectra have been resolved to several gaussian peaks, and these have been explained on the basis of vacancy-induced electronic states, crossover transitions advocated in molecular orbital theory and plasmon oscillation.

Keywords. X-ray emission; electronic states; plasmon oscillation.

1. Introduction

It is well known that inner shells of atoms when excited with high energy electrons or photons provide information about the unoccupied conduction states in a solid. The core-level processes are sensitive to final states as the initial states have narrow energy widths. In 3d transition metals excitation of 2p electrons can give information about the unoccupied 3d states (Acharya *et al* 1990, 1993). The electronic structure of 3d or 4d transition metal ions has been the subject of investigation both from theoretical as well as experimental view points, to arrive at the conclusion whether the metal acts as an electron donor or as an electron acceptor (Ramqvist *et al* 1969). Recently, the effect of vacancy production in the L X-ray spectra of carbide, borides etc of molybdenum has been studied (Acharya and Sakthivel 1994). Furthermore, it is well known that vacancy cascades are produced when an atom ionized in an inner shell de-excites through radiative or Auger transitions. Such vacancy cascades and their distribution in different shells like K, L and M influence the fluorescence yields of X-ray emission lines (Krause *et al* 1972; McGuire 1972a, b). Although X-ray photoelectron spectroscopy work on oxides of vanadium and molybdenum has been reported (Thole and Vander Laan 1987, 1988; Goering *et al* 1994), studies on powders and thin films of varying V_2O_5 and MoO_3 compositions have not been reported. Like many transition metal oxides, V_2O_5 and MoO_3 find extensive use in catalysts, intercalation

compounds, electrochromic applications and cathodic material for lithium batteries (Ballarin *et al* 1995; Ragot *et al* 1995). The electrochromic behaviour of V_2O_5 and MoO_3 thin films deposited by various methods has been reported to be highly structure-dependent, and the metal insulator transition in VO_x is very much complicated due to crystallographic changes taking place at transition (Huberts *et al* 1996). Thus, the present study has been taken up to investigate the electronic process taking place in this composite system of V_2O_5 and MoO_3 . A comparative study of the powders and the thin films deposited on glass substrates was carried out on $K_{\beta 1-3}$ emission line in order to correlate chemical shifts, asymmetry indices and line widths to vacancy distribution, density of electronic states and other electronic processes taking place in the system.

2. Experimental

Powders of V_2O_5 and MoO_3 , obtained by heating sodium vanadate and molybdic acid, respectively, were finely ground and mixed in definite proportions. The mixtures were then thoroughly homogenized by grinding in a ball mill, and pellets were prepared from these powders by application of one ton pressure in a pelletizing press. These pellets were annealed at 450°C for 2 h before being taken out for film deposition or X-ray emission study. Thin films of V_2O_5 , MoO_3 powders, and the different compositions of V_2O_5 – MoO_3 compounds were deposited on borosilicate glass plates by thermal evaporation in vacuum (10^{-3} Pascal). Prior to X-ray-emission spectral

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study, all the samples were characterized by X-ray powder diffraction. X-ray emission spectra of the samples were recorded with a Philips PW-1400 wavelength dispersive spectrometer system having scandium X-ray tube operating at 50 kV 60 mA. $K_{\beta 1-3}$ -emission spectra of vanadium were recorded by analysing crystal of LiF (200), and using the flow proportional counter as detector. All these spectra were recorded in vacuum. The scanning speed employed for (continuous mode) this purpose was $0.25^\circ 2\theta \text{ min}^{-1}$ with a chart speed of 8 cm min^{-1} . The spectra were also recorded in the step-scanning mode with a step of $0.005^\circ 2\theta$ angle. The counting time during step scanning was selected depending upon the number of counts recorded at the peak position so as to have minimum standard deviation and, generally for $K_{\beta 1-3}$ line, the time chosen was 5 sec at each step. A flow proportional counter with predetermined peak height discrimination was used for recording $K_{\beta 1-3}$ spectra of vanadium in the angular range of 68 to 70 degree on a LiF (200) face in first order. The experimental error on $K_{\beta 1-3}$ shift was $\pm 0.027 \text{ eV}$ in energy scale or $\pm 0.005 2\theta$ in 2θ scale. The resolution of the detector was found to be 15% at vanadium peak position, as found out from pulse-height-distribution curve using appropriate counting time. All data were smoothened with an exclusive programme

developed by the authors. The programme utilizes binomial distribution function for 5 channel smooth (Jenkins *et al* 1995). The first- and second-differential curves of the original smoothened data gave an idea about the number of peaks and their positions in the emission spectra. Subsequently spectra were fitted with various peak shapes like lorentzian, voigtian, pseudo voigtian, gaussian and pearson VII function. The best fit was obtained for gaussian shape taking into consideration the physical process occurring in the system.

3. Results

Figure 1 shows the X-ray diffractograms of thin ($t \approx 240 \text{ nm}$) and thick ($t \approx 480 \text{ nm}$) films. The thin film has been found to be more crystalline compared to the thick film. In thick film, two low intense reflections appear compared to the thin film. Similar behaviour for films of $\text{V}_2\text{O}_5\text{--MoO}_3$ system with varying compositions has also been observed (not reported in this investigation). The annealed powders of $\text{V}_2\text{O}_5\text{--MoO}_3$ were subjected to X-ray powder diffraction and these data were analysed with LSUCRIPC programme for structure determination. Table 1 shows the structural parameters for the range of

Figure 1. X-ray diffraction of $\text{V}_2\text{O}_5\text{--MoO}_3$ thin and thick film deposited over glass plate.

Table 1. Lattice parameters and axial ratio of V_2O_5 - MoO_3 -annealed powders of different compositions as calculated from X-ray powder diffraction data.

Sample composition	Lattice constants ($\text{\AA}$)			Axial ratio c/a	Angles (degree)			Crystal class
	a	b	c		α	β	γ	
V_2O_5	4.38	11.45	3.59	0.82	94.88	95.08	89.57	Orthorhombic
V_2O_5 -23.0 at wt% MoO_3	8.74	11.01	4.42	0.51	91.41	95.28	90.64	
V_2O_5 -54.0 at wt% MoO_3	9.24	10.50	4.26	0.46	99.06	102.34	88.07	
V_2O_5 -87.0 at wt% MoO_3	7.07	11.67	6.64	0.93	89.95	95.41	104.67	
MoO_3	6.99	14.01	2.89	0.41	92.38	92.67	97.14	

composition of V_2O_5 - MoO_3 powders. All the composite powders were found to be orthorhombic with the axial ratio (c/a) maximum for 87 wt% of MoO_3 powder.

In figure 2 the $K_{\beta 1-3}$ emission spectra of vanadium in the thin film and powders have been given. The low energy and high energy tailing of these emission bands as well as the presence of shoulders in these regions lead us to believe the emission peaks to be envelope of two or three peaks depending upon the samples and the physical processes occurring in the system. Thus a first-order differential curve for this band was constructed which gave the preliminary idea about the composition of the band. The asymmetry indices, $\alpha = \text{low-energy side width} / \text{high-energy side width at } 3/4\text{th height of the bands}$, were calculated following the procedure of Pessa (1977). The asymmetry indices (table 2) were found to be more than unity which confirms the multiband structure of the emission peak. Thus all these emission bands were resolved by using curve fitting procedure where all possibilities like voigt, lorentzian, gaussian, pseudo voigt, pearson VII functions were fitted, and the best fit was taken with due consideration to the physical processes taking place in the system. The bands thus resolved are given in figures 3a and 3b which show the representative curves for thin film and powder systems. The details of such emission band position have been given in table 3.

4. Discussions

The development of molecular orbital approach and availability of shake-off probabilities along with transition rates of radiative Auger and Coster-Kronig processes have added a new dimension to the interpretation of complete K and L spectra of transition metals (Urch 1970; Krause *et al* 1972; McGuire 1972). In our earlier studies (Nayak *et al* 1988; Acharya *et al* 1989) on the sulphur K_{α} emission in thin films of Bi_2S_3 -CdS and Bi_2S_3 -PbS, we have explained the intensities of satellite emission bands on the basis of molecular orbital (MO) theory. However, MO theory is always not sufficient for samples involving transition metals. Vanadium $K_{\beta 1-3}$ spectrum (thin film)

Figure 2. Vanadium $K_{\beta 1-3}$ emission spectra in V_2O_5 - MoO_3 systems.

consists of a strong asymmetric peak at the highest emission energy followed by low and high energy tailings. Resolution of the composite band by curve fitting procedure depicts three peaks centring around 5417.63, 5409.94 and 5451.72 eV. The top of the spectrum, which corresponds to the transitions from valence band maximum (VBM) to $1s$, is ill defined due to superimposition of two other bands in the low and high energy side. The high energy side peak may be due to radiative decay of core exciton as predicted for Al in AlAs (Vergand *et al* 1989).

As seen from the table, the low energy satellite peaks show more intensity compared to the $K_{\beta 1-3}$ main emission line in all these compounds, which can be explained in the light of number of unpaired $3d$ electrons in these compounds. Tsutsuimi *et al* (1976) have explained the high intensity ratio of $K_{\beta'}/K_{\beta 1-3}$ line taking into consideration the number of unpaired electron in Mn compounds. Anomalous L_3/L_2 white line ratio in $3d$ transition metals from 0.7 : 1 for Ti to 3 : 1 in Fe and Ni have been explained by Leapman *et al* (1982) by taking into account the many electron effects in thin films. Senemaud *et al* (1991) have explained the observed L_3/L_2 peak intensity ratio of 4 : 1 in terms of increased level (L_2) width. This effect arises in $3d$ transition metals since Coster-Kronig decay channels give a shorter L_2 -hole life time relative to L_3 -hole life time. Another source of core-level broadening is multiplet splitting of the core states by their interaction with unpaired vacant $3d$ states. Data from XPS studies indicate that this effect produces asymmetrical shoulders on L_3 and L_2 peaks. It has been observed

Table 2. Summary of the results of curve fitting by curve fit on vanadium $K_{\beta 1-3}$ of thin films and powder samples of V_2O_5 - MoO_3 . Peaks were assumed to be Gaussian.

Type of sample	Composition	VK _{$\beta 1/3$} (eV)	Low energy satellite (eV)	High energy satellite (eV)
Powder	V_2O_5	5418.47 (100)	5415.67 (171)	5421.07 (44.5)
	V_2O_5 -23.0 at wt% MoO_3	5419.53 (100)	5416.17 (187)	5421.77 (42)
	V_2O_5 -54.0 at wt% MoO_3	5418.95 (100)	5415.72 (168)	5422.12 (40)
	V_2O_5 -87.0 at wt% MoO_3	5418.37 (100)	5410.86 (93.0)	Not observed
Thin film	V_2O_5	5417.63 (100)	5409.94 (241)	5451.72 (12)
	V_2O_5 -23.0 at wt% MoO_3	5417.53 (100)	5409.32 (181)	5433.01 (14)
	V_2O_5 -54.0 at wt% MoO_3	5418.90 (100)	5402.58 (421)	Not observed
	V_2O_5 -87.0 at wt% MoO_3	5414.41 (100)	5381.73 (10)	Not observed

Relative intensities are given in brackets

that core levels accessible for study with above 1 keV photons, Auger process is the predominant mechanism of vacancy filling. Coster-Kronig process and shake off contribute equally to the spectrum (Acharya and Sakthivel 1994). Generally the satellite contributions vary with initial vacancy distribution. In general Coster-Kronig satellites appear in the high energy side of diagram line and shake-off satellites coincide with the diagram line (Ivanovskii *et al* 1987). However, competitive decay of individual holes in multi-hole configuration leads to transfer of a fraction of high energy satellites to the region beneath the parent line. This will enhance the FWHM of the line as well as the intensity of high energy side satellite line (Jia *et al* 1992).

$K_{\beta 1-3}$ emission spectra ($3p_{3/2} \rightarrow 1S$) in powders and thin films depict the emission bands to have high energy tailing, together with the presence of nondiagram satellite line. In case of transition metal alloys, hybridization of p - d and d - d bands can affect the local density of states (LDOS), which in turn can change the number of states of the constituent atoms, and the respective potential need to be realigned with respect to each other so as to minimize charge transfer. This hybridization is sensitive to composition and arrangements. In case of TiO_2 , it has been observed that a chemical shift of core level by ~ 2 eV is due to charge transfer from Ti to oxygen, which has been attributed to core excitons in TiO_2 (Brown *et al* 1977). Furthermore, the d - d overlap results in a bonding-antibonding region within the transition metal itself. Thus the d band filling will introduce an exchange interaction with the $3p$ level, thereby causing greater overlap with $3d$ bands. Such type of overlap has been observed for TiO_2 in X-ray absorption and UV photoelectron spectra (Citrin *et al* 1979; Bruhn *et al* 1979) which have been explained on the basis of exchange interaction and many electron effects. Thus the high energy tailing or satellite peak structure of thin films and powders can be explained in considering the many electron effects and charge transfer processes taking place in the system (Meisel *et al* 1989).

Table 3. $K_{\beta 1-3}$ emission peak position and asymmetry indices (α) of vanadium in powders and thin films of V_2O_5 - MoO_3 compound.

Sample composition	Powder peak position (eV)	Asymm. index (α)	Thin film peak position (eV)	Asymm. index (α)
V_2O_5	5418.16	1.13	5414.45	1.28
V_2O_5 -23.0 at wt% MoO_3	5418.16	1.0	5414.45	1.06
V_2O_5 -54.0 at wt% MoO_3	5417.59	1.08	5404.01	1.0
V_2O_5 -87.0 at wt% MoO_3	5417.03	1.08	5413.36	1.04

Figure 3a. Decomposition of $K_{\beta 1-3}$ spectra in V_2O_5 - MoO_3 thin films.

Figure 3b. Decomposition of $K_{\beta 1-3}$ spectra in V_2O_5 - MoO_3 powder.

Thus from the above observation and discussions we are led to believe that (i) stoichiometry and crystal structure have a profound influence on $K_{\beta 1-3}$ line of vanadium compounds and thin films, (ii) the change in intensities of $K_{\beta 1-3}$ and other satellite peaks can be explained on the basis of production of vacancies, core-hole life time and Coster-Kronig processes taking place in these compounds and thin films and (iii) many electron effects and exchange interaction between d and p states

can also influence the emission spectra, and the deviation in the relative intensity of these $K_{\beta 1-3}$ and satellite bands can be explained on this argument.

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