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AUGER ELECTRON SPECTROSCOPY INVESTIGATIONS OF THE SURFACE CHEMICAL COMPOSITION OF VANADIUM, THE VANADIUM OXIDES, AND OXIDIZED VANADIUM: CHEMICAL SHIFT AND PEAK INTENSITY ANALYSIS

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AUGER ELECTRON SPECTROSCOPY INVESTIGATIONS OF
THE SURFACE CHEMICAL COMPOSITION OF VANADIUM, THE VANADIUM OXIDES,
AND OXIDIZED VANADIUM: CHEMICAL SHIFT AND PEAK INTENSITY ANALYSIS

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ABSTRACT

The Auger spectra of vanadium metal and of the oxides $V_0^{0.92}$, $V_2O_3$, and $VO_2$ have been studied. Chemical shifts on the order of 0.6 eV per oxidation number have been observed for the vanadium inner shell Auger transitions. Relative intensities of the oxygen and vanadium Auger peaks could be used to determine the surface composition of the different oxides. Using both the chemical shifts and the oxygen to vanadium Auger peak intensity ratios for the different vanadium oxides, the oxidation of vanadium metal to $VO$ and then to $V_3O_5$ with increasing temperature was observed.
I. INTRODUCTION

Definitive interpretation of many surface phenomena on an atomic level often requires knowledge of the chemical composition of the surface and the oxidation state of surface atoms. Auger Electron Spectroscopy (AES) can detect the presence of impurities on surfaces at a concentration level of $10^{13}$ atoms/cm$^2$ (that is, coverages on the order of 1-5% of a monolayer). Although most investigations have used AES to provide qualitative surface chemical analysis, it has also been demonstrated that the technique can be calibrated to yield quantitative data on the surface composition.

There have been several reports that indicate a shift in the energy of various Auger transitions upon a change in the oxidation state of an atom. In the light of the success of photoelectron spectroscopy (ESCA) in measuring single state, inner shell electron binding energy shifts with changes of oxidation state, it seemed likely that inner shell Auger transitions could also be used to probe the chemical state of the surface atoms. To a first approximation, the measured energy of a $W_{O}^{X_{Y}}$ Auger transition is

$$
\overline{E}_{W_{O}^{X_{Y}}} (Z) = \overline{E}_{W_{O}} (Z) - \overline{E}_{X_{p}} (Z) - \overline{E}_{Y_{q}} (Z+\Delta) - \phi_{A} \tag{1}
$$

where

$$
\overline{E}_{W_{O}^{X_{Y}}} (Z) \equiv \text{the measured mean energy of a } W_{O}^{X_{Y}} \text{ Auger transition electron ejected from an atom of atomic number } Z.
$$
the mean binding energies (relative to the Fermi level) of the $W_o$, $X_p$, and $Y_q$ energy levels respectively

$\Delta \equiv$ effective incremental charge

$\phi_A \equiv$ the work function of the electron energy analyzer

If the atom is placed in different chemical environments one would expect shifts in the energy of the ejected Auger electron due to the shifts of each of the energy levels. According to Eq. (1), the chemical shifts of Auger electrons from inner shells should be of the same magnitude as the shifts in the binding energy of photoelectrons for the same system. The Auger shifts will be determined by the following equation:

$$\Delta_{W^X^Y}^{o\ p\ q} (Z) = \Delta_{W^o} (Z) - \Delta_{X^p} (Z) - \Delta_{Y^q} (Z+\Delta) \quad (2)$$

where

$\Delta_{W^X^Y}^{o\ p\ q} (Z) \equiv$ the shift in the energy of the $W^X^Y$ transition Auger electron

$\Delta_{W^o} (Z), \Delta_{X^p} (Z), \Delta_{Y^q} (Z+\Delta) \equiv$ the chemical shifts in the binding energies of the $W^o$, $X^p$, and $Y^q$ levels respectively.

An analysis of the chemical shifts of an inner shell Auger transition, after suitable calibration, should permit one to determine not only the oxidation state of atoms at the surface but also changes of oxidation state during the course of a surface chemical reaction.
In this paper, we report on studies of the Auger spectra of vanadium metal and of various vanadium oxides: V\textsubscript{0.92}, V\textsubscript{2}O\textsubscript{3}, and V\textsubscript{O}\textsubscript{2}. We have observed chemical shifts of the inner shell vanadium Auger transitions on the order of electron volts upon changes of the oxidation state of vanadium. We have also found that the ratio of the oxygen to vanadium Auger peak intensities in the compounds studied can be used for quantitative determination of the chemical composition at the surface. Finally, using the observed chemical shifts and oxygen to vanadium Auger peak intensity ratios of the different vanadium oxides, the oxidation of vanadium metal was monitored as a function of temperature and the oxidation state of the vanadium atoms was observed to increase with temperature.

II. EXPERIMENTAL

A stainless steel ultra-high vacuum apparatus that can be used for both AES and low energy electron diffraction (LEED) studies of surfaces was used in this investigation. Experimental pressures of $1 \times 10^{-9}$ torr were achieved using ion and titanium sublimation pumping. The AES-LEED chamber contained facilities for sample manipulation, noble gas ion bombardment, electron bombardment and/or resistance heating of the sample(s), and a manifold-leak valve suitable for the introduction of pure gases into the system. The retarding field energy analyzer was a four-grid electron optics (obtained from Varian Associates) which also contained the normal incidence electron gun used for low energy electron diffraction. Although the chamber was also fitted with a high voltage-high current oscilloscope gun (Model 3WP1) placed at a 75° angle with respect to normal incidence, the LEED gun was used to produce the inner shell
electron vacancies necessary to initiate the Auger process because of its better beam definition at the target surface. The gun was operated with a 1 kV accelerating voltage and its filament was heated using a stable d.c. power supply. The working principles and the electronics of the retarding field energy analyzer in AES has been described in detail elsewhere. In brief, (1) an extensively modified Varian Auger Analyzer (Model 981-0538) supplied the d.c. ramp voltage with the superimposed a.c. modulation and contained a capacitance neutralization device in its analyzing circuit, (2) a PAR HR-8 amplifier provided the lock-in detection, and (3) the results were recorded using an X-Y recorder.

Typical conditions for the chemical shift studies of the vanadium oxides were: the amplitude of the a.c. modulation was 3.0 volts peak-to-peak, the d.c. ramp voltage scan rate was 1.5 volts/minute, and the PAR time constant was 1 second. These conditions assured that the output voltage of the analyzer circuit reached a steady-state value for each 0.1 volt range scanned.

The second derivative technique (resulting in a $d^2I/dV^2$ vs. $V$ plot, where $I$ is the current to the collector at the retarding grid voltage $V$) was employed in the measurements because of the proximity of the vanadium $L_2$ and $L_3$ energy bands which makes the determination of the $dI/dV$ peak maximum difficult. The chemical shifts were measured on the $d^2I/dV^2$ graph at the high energy minimum of the Auger peak. This procedure is equivalent to measuring the $dI/dV$ peak maximum as long as the peak shape on the high energy side remains constant. The intensity contained within a $dI/dV$ peak has been shown to be proportional to the peak-to-peak height of the $d^2I/dV^2$ trace. Since the low energy side of the Auger
peaks were often distorted due to the overlapping of peaks and to inelastic energy loss processes, we used the half-peak height to the high energy minimum of the $d^2I/dV^2$ peak as an indicator of the peak intensity.

The vanadium metal single crystal was obtained from Metals Research Corp, oriented to ±$1^\circ$ of the (100) plane using the back-reflection Laue X-ray technique, spark cut, mechanically polished, and etched prior to spot welding it onto the polycrystalline vanadium holder which was attached to the manipulator. The $V_{0.92}$ and $V_{2.03}$ crystals were obtained from and characterized by Lincoln Laboratories and Semi-Elements Corp, respectively. They were polished to yield a smooth surface and etched. The $V_{2.03}$ and $V_{0.2}$ powders (from Research Organic/Inorganic Corp.) were hydrostatically pressed into a wafer form for ease in mounting on the sample holder. The resistivities of these pressed powders (due mainly to grain boundary effects) were on the order of $10^3$ ohm cm. Two of these pressed powder samples were etched while the other two were untreated. The oxides were wrapped in vanadium foil, leaving only the area to be probed exposed; the foil was then spot welded to the sample holder.

After a 150°C bakeout of the vacuum chamber, the samples were typically cleaned in situ by bombardment with 300 volt Argon ions (5-10 μA for 30 minutes) followed by annealing at temperatures varying from 300-700 °C.
III. RESULTS

A. Vanadium Metal

The vanadium (100) metal surfaces that had been ion bombarded and underwent a mild heat treatment as described above displayed the (1x1) diffraction pattern that is expected from the projection of the bulk unit cell. Upon annealing at 1200°C for 10 minutes, this (1x1) pattern was transformed into a c(2x2) pattern. The additional spots are believed to be caused by sulfur which is by far the major impurity present in vanadium metal, and which segregates to the surface upon heating. Although the vanadium samples used had been subjected to intensive cleaning treatment (i.e., ion bombardment-annealing cycles and high temperature oxygen and hydrogen treatments), neither the sulfur Auger peak nor the c(2x2) surface structure could entirely be eliminated although both were markedly decreased in intensity.

The electron configuration of the neutral vanadium atom is [Ar] 4s^2 3d^3, and the energy level scheme is shown in Fig. 1. The inner shell levels have been determined using ESCA^{8,11} and are on the order of 0.5 eV wide.^{12} The valence band consists of a mixture of the 4s and 3d states, and it has been calculated to be 6.8 eV wide^{13} and to contain high optical density of states peaks at 0.6 eV and 1.6 eV below the Fermi level.^{14}

The dI/dV and d^2I/dV^2 Auger spectra of vanadium metal are shown in Fig. 2. Our results agree with the previously published Auger spectra of vanadium,^{11,15} and the transitions to which the peaks have been assigned are shown in the figure. The transitions that were monitored in the studies of the chemical shifts of the vanadium oxides are those labeled L^2 M_{2,3}^M, M_{2,3}^M, and L_{2,3}^M, V. These were chosen because they (1) are
the most intense peaks in the high energy part of the Auger spectrum, and
(2) are characteristic of the two different types of Auger transitions:
the first \((L_{2}M_{2,3}M_{2,3})\) involves a transition in which all of the parti-
cipating energy levels are inner shells, while the second \((L_{2}M_{2,3}V)\) transi-
tion involves the valence band. The peak intensity analysis was carried out
using the vanadium \(L_{2}M_{2,3}V\) transition and the oxygen \(KVV\) transition (not
shown). The low energy \(M_{2,3}VV\) transition would be expected to be quite
sensitive to the chemical state of the vanadium atoms which are at the
surface. This peak has also been monitored and the results will be discuss-
ed in another paper.

B. Chemical Shifts in the Vanadium Oxides

The energy of the vanadium \(L_{2}M_{2,3}M_{2,3}\) inner shell Auger transition
was observed to vary smoothly as a function of the oxidation state of the
vanadium cation. All measurements were made relative to the energy of
the vanadium metal transition in order to eliminate errors due to long-
term instrumental drift and spectrometer work function changes. In Fig. 3
the shift of the \(L_{2}M_{2,3}M_{2,3}\) Auger transition is plotted as a function of
the oxidation number of vanadium in the various oxides. The chemical
shifts are also listed in Table I. The probable error as determined
statistically is \(\pm 0.15\) eV. The \(L_{2}M_{2,3}M_{2,3}\) transition exhibited a \(-0.6\) eV
shift (on the average) per oxidation number. The other inner shell transi-
tions were observed to shift in the same manner (i.e., in both magnitude
and direction) although their shifts have not been carefully monitored.

The energy of the \(L_{2}M_{2,3}V\) valence band Auger transition appears to
vary anomalously in the vanadium oxides studied. The results are contain-
ed in Table I. The chemical shift of this valence band transition is in
the direction of higher Auger electron energy for the $V_{0.92}$ and $V_2O_3$ samples (relative to vanadium metal) while it is in the direction of lower energy for the $VO_2$ samples.

Although the shapes of the Auger peaks were not rigorously monitored, no change in shape on the high energy side of the $L_2M_{2,3}M_{2,3}$ and $L_2M_{2,3}V$ peaks was detected in the course of these experiments. It should also be noted that the $V_2O_3$ single crystal and $V_2O_3$ pressed powder samples gave identical results throughout these experiments.

C. Oxygen and Vanadium Auger Peak Intensity Ratios

The half-peak height ratios, $h_0/h_V$, of the oxygen KVV and the vanadium $L_2M_{2,3}V$ transition peaks in the different vanadium oxides were measured as described above. The results are shown in Fig. 4. The intensity ratios vary smoothly with the vanadium oxidation number. The statistically averaged results are displayed in the first numerical column of Table II, the probable error being $\pm(0.10-0.15)$ units. The second column (labeled EXP.) shows the results normalized to the $VO_2$ ratio, assuming that the $VO_2$ is stoichiometric and that the experimentally determined intensity ratio reflects this 2:1 $O/V$ ratio. The third column (CALC.) shows the calculated oxygen/vanadium ratios of the various compounds again normalized to $VO_2$, assuming that the stoichiometry near the surface for each oxide is that given by the chemical formula.

It was observed that the low energy sides of the Auger peaks from the oxides displayed a definite "tailing" effect relative to the peaks observed from the vanadium metal surface. Also, $V_2O_3$ again gave similar results for the single crystal and pressed powder samples.
D. Oxidation of the (100) Vanadium Crystal Surface

After establishing the Auger spectrum for the "clean" metal surface, the vanadium (100) crystal face was oxidized using the temperature range 25-1200°C and the pressure range $10^{-7}$-$10^{-2}$ torr. The exposure generally varied from $10^2$-$10^7$ L ($1L = 10^{-6}$ torr sec). The oxygen/vanadium intensity ratio was monitored after each exposure, as was the position of the $L_{2,3}M_{2,3}$ peak. The position of the reference (i.e., clean vanadium) peak was established after heating the crystal to 1000°C in vacuum for 2 minutes - this heat treatment being sufficient to restore the Auger trace which is characteristic of unoxidized vanadium metal. Using this procedure, one can eliminate any error due to a work function change of the energy analyzer during the oxygen adsorption. In those experiments where the vanadium reference peak was monitored both before and after the oxygen exposure, the detected work function change, $\Delta \phi_A$, was on the order of 50 mv. Using the chemical shifts and the oxygen/vanadium peak intensity ratios obtained from the vanadium oxides as reference points, Fig. 5 shows a plot of the observed chemical shifts vs. the oxygen/vanadium peak intensity ratios obtained after the oxidation runs. The data points clustered below the $V_0^{0.92}$ reference point are the results of runs carried out at 25°C and in the pressure range $10^{-7}$-$5 \times 10^{-4}$ torr. These results show that the product formed is in the oxygen-deficient part of the VO solid solution range and has an approximate composition of $V_0^{0.8}$. The single point above the $V_0^{0.92}$ reference point was obtained after oxidation at a temperature around 75°C and a pressure of $3 \times 10^{-4}$ torr; it corresponds to a chemical composition of $V_0^{1.1-1.2}$ (i.e., in the oxygen-
rich part of the VO solid solution range). The point near the \(V_2O_3\) reference was obtained after a 150°C oxidation run at a pressure of \(2 \times 10^{-4}\) torr. Those points clustered between the \(V_2O_3\) and \(VO_2\) reference points resulted from runs in the temperature range of 400-1200°C and at pressures in the range \(5 \times 10^{-4}-5 \times 10^{-3}\) torr; they suggest the formation of an oxide layer with a chemical composition corresponding to \(VO_{1.6-1.7}\). Since these Auger peaks did not appear to be broadened with respect to those obtained from the known oxides, it seems unlikely that these data points are the result of the formation of a mixture of \(V_2O_3\) and \(VO_2\).
IV. DISCUSSION

The chemical shifts (relative to vanadium metal) of the inner shell vanadium $L_{2,3}M_{2,3}$ Auger transition peak in the vanadium oxides studied correspond to a change in energy of approximately 0.6 eV per vanadium oxidation number. These shifts are in the direction of increasing binding energy of the energy levels involved with respect to their position in vanadium metal. Such a shift toward increased binding energy is to be expected from elementary bonding considerations: the electron charge transfer upon bonding is from the vanadium to the more electronegative oxygen atoms, and the subsequent increase in the effective nuclear charge on the vanadium causes the inner shell energy levels to shift in the direction of higher binding energy. The magnitude of the shift per vanadium oxidation number is not constant, being 0.52, 0.58, and 0.64 eV for $V^{2+}$, $V^{3+}$, and $V^{4+}$ respectively. This variation is expected since the increase in the effective nuclear charge should not be linear with each successive incremental electron charge transfer. Both the magnitude and direction of the observed chemical shifts are compatible with those observed for single inner shell energy levels using photoelectron spectroscopy.

Using X-ray emission techniques, Fischer has determined that the vanadium $L_3$ level shifts $-1.9$ and $-2.4$ eV in $V_2O_3$ and $VO_2$ respectively relative to vanadium metal. Combining our data on the shift of the $L_{2,3}M_{2,3}$ Auger peak in these compounds with that obtained by Fischer for the $L_3$ level and making the reasonable assumption that the $L_2$ and $L_3$ levels shift equally, the chemical shift of the $M_{2,3}$ level may be
estimated. A simple calculation shows that the M\textsubscript{2,3} level shifts -1.8 and -2.5 eV in V\textsubscript{2}O\textsubscript{3} and VO\textsubscript{2} respectively. That is, the M\textsubscript{2,3} shift is equal to the chemical shift of the L\textsubscript{3} level, within the experimental uncertainty. This result is in agreement with those obtained by photoelectron spectroscopy for core-level electrons.\textsuperscript{8} Thus, the data strongly suggests that the vanadium M\textsubscript{2,3} level may be treated as an inner shell despite its proximity to the valence band.

The valence band vanadium L\textsubscript{2}M\textsubscript{2,3} V Auger transition peak exhibits a small chemical shift and behaves markedly different from the inner shell Auger transitions in its dependence on the vanadium oxidation number. The seemingly anomalous behavior of this peak may be attributed to the fact that the transition involves the valence band. As the result, the peak position will be influenced by (1) the variation in the density of states of the vanadium valence band due to the change in crystal structure and the transfer of electrons from this level to the oxygen atoms, (2) the interaction of the oxygen valence electron energy states with the vanadium valence states, and (3) the chemical shifts of the inner shells. Since the L\textsubscript{2} and M\textsubscript{2,3} chemical shifts are of nearly the same magnitude, their net contribution to the shift of the L\textsubscript{2}M\textsubscript{2,3} V peak will approach zero and any observed shift will be mainly due to the changes occurring in the valence band. Because VO\textsubscript{2} is the only one of these oxides that was in its semiconducting state (i.e., below its semiconductor-to-metal transition temperature) at room temperature,\textsuperscript{17} it is possible that the Auger spectra are displaying the consequences of this temperature-dependent transition. This could explain the -0.7 eV
shift between VO$_2$ and the other oxides. The observed shift is in the proper direction and of the right order of magnitude to be explained in this manner.\textsuperscript{17} It is unlikely that space charge at the surface causes this shift since the conductivity of semiconducting VO$_2$ is relatively high (approximately $10^{-1}$ ohm$^{-1}$ cm$^{-1}$);\textsuperscript{18} also, the trend in the inner shell Auger transition results argues against the existence of a space charge effect. Experiments are currently in progress to further investigate the effect of the semiconductor-to-metal transitions on the Auger spectra.

The variation of the Auger peak intensity ratio, as seen in the columns labeled EXP. and CALC. in Table I, indicates that the surface composition of the vanadium oxides reflects the bulk composition within the experimental error. The observation that bombardment by the electron beam does not cause a detectable change in the stoichiometry of the vanadium oxides is in agreement with Fischer's data. Therefore, it appears that the non-destructive calibration of a chemical system can be carried out using AES, and the intensity ratio determination appears useful in ascertaining the chemical composition of a surface layer.

The studies of oxidation of the vanadium metal surface have provided the opportunity to investigate to what extend Auger chemical shifts and/or peak intensity ratio measurements can be used to monitor the changes of chemical composition and of oxidation states during a chemical surface reaction. Oxidation at room temperature yielded compounds with structures in the VO solid solution range. The results indicate that for the oxygen exposures used ($\geq 10^2$ L) a homogeneous surface layer of the oxide is
being formed. The layer must be at least 5 monolayers thick.\textsuperscript{19} It should be noted that the structural rearrangement of the b.c.c. vanadium metal to accommodate the oxygen atoms in the VO crystal lattice should not be too difficult since VO has a f.c.c. structure.\textsuperscript{17} The higher vanadium oxides, however, have more complex crystal structures, and the energy available at 25°C may not be sufficient to form these structures.

It is perhaps surprising that the high-temperature oxidation of vanadium metal did not produce VO\textsubscript{2}. V\textsuperscript{4+} being the most stable of the vanadium oxidation states. However, an investigation of the phase equilibria in the V\textsubscript{2}O\textsubscript{3} - VO\textsubscript{2} system by Katsura and Hasegawa demonstrated that the V\textsubscript{3}O\textsubscript{5} Magneli phase is formed when the system is heated to high temperatures in oxygen partial pressures in the range 3.3 \times 10^{-4} - 9.6 \times 10^{-3} \text{ torr}.\textsuperscript{20} Since our experiments which yielded a composition on the order of VO\textsubscript{1.6-1.7} (i.e., V\textsubscript{3}O\textsubscript{4.8-5.1}) were carried out in this oxygen pressure range, it appears likely that we are observing the formation of this particular Magneli phase. The lack of noticeable broadening of the vanadium L\textsubscript{2}M\textsubscript{2,3} M\textsubscript{2,3} Auger transition peak also indicates the presence of a surface layer in which all of the vanadium atoms are in the same oxidation state, as they are in this defect structure\textsuperscript{21} of VO\textsubscript{2}. In the case of the formation of a mixture of oxides (V\textsubscript{2}O\textsubscript{3} and VO\textsubscript{2}), a broadening of the vanadium Auger peaks would be expected.

Furthermore, we observed the formation of a compound with the composition of V\textsubscript{2}O\textsubscript{3} when oxidation was carried out at an oxygen pressure just within the range (<3.3 \times 10^{-4} \text{ torr}) where Katsura and Hasegawa prepared V\textsubscript{2}O\textsubscript{3} in bulk quantities. Therefore, our results support their
data on the oxygen pressure dependence of the formation of $V_2O_3$ and $V_3O_5$.

These results indicate that the observation of chemical shifts and intensity ratios of Auger transition peaks by Auger Electron Spectroscopy is useful for the determination of and for following changes in the oxidation states of surface atoms and the chemical composition of surfaces.
Table I. The chemical shifts of the vanadium \(L_2M_{2,3}M_{2,3}\) and vanadium \(L_2M_{2,3}V\) Auger transitions in the vanadium oxides (relative to vanadium metal).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta_{L_2M_{2,3}M_{2,3}})</th>
<th>(\Delta_{L_2M_{2,3}V})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{VO}_0.92)</td>
<td>-0.95 eV</td>
<td>+0.30</td>
</tr>
<tr>
<td>(\text{V}_2\text{O}_3)</td>
<td>-1.75</td>
<td>+0.35</td>
</tr>
<tr>
<td>(\text{VO}_2)</td>
<td>-2.55</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

Table II. The oxygen KVV to vanadium \(L_2M_{2,3}V\) Auger half-peak height ratios in the vanadium oxides. The results are normalized to the \(\text{VO}_2\) ratio (EXP.) and compared with the values calculated from the chemical formulae (CALC.).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(h_0/h_V)</th>
<th>EXP.</th>
<th>CALC.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{VO}_0.92)</td>
<td>1.23</td>
<td>0.50</td>
<td>0.46</td>
</tr>
<tr>
<td>(\text{V}_2\text{O}_3)</td>
<td>1.78</td>
<td>0.73</td>
<td>0.75</td>
</tr>
<tr>
<td>(\text{VO}_2)</td>
<td>2.45</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

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REFERENCES

FIGURE CAPTIONS

Fig. 1 Schematic representation of the energy scheme of vanadium metal.

Fig. 2 dI/dV and d²I/dV² Auger spectra of a vanadium (100) metal surface.
Primary electron energy: 1000 eV. Peak-to-peak modulation: 3.0 v.

Fig. 3 The chemical shift of the vanadium $L_{2,3}M_{2,3}$ Auger transition in the vanadium oxides as a function of the vanadium oxidation number.

Fig. 4 The oxygen KVV to vanadium $L_{2,3}V$ Auger transition half-peak height ratios in the vanadium oxides as a function of the vanadium oxidation number.

Fig. 5 The chemical shift of the vanadium $L_{2,3}M_{2,3}$ Auger transition as a function of the oxygen KVV to vanadium $L_{2,3}V$ half-peak height ratio for the vanadium metal oxidation runs. The known vanadium oxides are used as reference points.
Fig. 2
Fig. 3

- $\Delta$ eV vs Oxidation Number

- $V_2O_3$
- $Vo_{0.92}$
- $Vo_2$

XBL 7111-7645
Fig. 4
Fig. 5
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