Auger Analysis of Scandium, Sc-Oxide, Sc-Deuteride and Sc-Nitride*

G. Moore
General Electric Company, Neutron Devices Department
Largo, FL 34294-2908

and

G. C. Nelson and H. H. Madden
Sandia National Laboratories
Albuquerque, NM 87185

ABSTRACT

Elemental scandium, Sc-oxide, Sc-hydride and Sc-nitride films were investigated using Auger electron spectroscopy in a study of the interaction of scandium with hydrogen and atmospheric gases. A catalog of Sc Auger spectra representative of Sc-metal, Sc-O, Sc-H and Sc-N bonding is presented. Changes in spectral features unique to the changes in scandium matrix are identified. Comparisons with theoretical calculations, along with variation in the experimental conditions for recording the Auger data, enabled the Sc spectra found in separate low and high energy regions to be identified with M-shell and L-shell core excitations, respectively.

*This work supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00656 and Contract No. DE-AC04-76DP00789.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ph*

MASTER

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

I. Introduction

Scandium hydride is a metal-hydrogen system which has been found useful for hydrogen storage. Hydrogen storage in metals is known¹ to be more efficient than in liquid hydrogen in terms of the number of hydrogen atoms stored per unit volume, while much less efficient, if one neglects packaging, than liquid hydrogen in terms of hydrogen weight percent in the storage system. The "loading" and "unloading" of a bulk hydride storage system obviously occurs through the surface of the metal sample, and the surface chemistry of the system is therefore important. Furthermore, scandium atoms which are strongly bonded to impurities such as oxygen and carbon decrease the net efficiency of a scandium sample in the storage of hydrogen.

Auger electron spectroscopy (AES) is commonly used for the analysis of surfaces of metals such as scandium. In most such uses, information only on elemental surface composition is sought. Because no direct (characteristic) signal from hydrogen is seen in any electron spectroscopy, these spectroscopies are commonly described as "blind" to hydrogen. In surface systems where hydrogen is an important constituent this "blindness" means that AES (in its normal mode of use) is an ineffective probe of the surface. Evidence for surface hydrogen can be found in Auger data however, in the form of hydrogen-induced changes in the Auger signals from the host material. Chemically bonded surface impurities such as oxygen and nitrogen also cause changes in the Auger line shapes of the host material - usually to a far greater extent than does hydrogen. Thus, if AES is to be used to probe the surface of hydrogen-containing multicomponent systems, a cataloging of the effects of each individual component on the Auger line shapes for the host material should be made. This paper reports such a catalog of the effects of oxygen, nitrogen and hydrogen on the Auger spectra for scandium.

A line shape study on the effects of hydrogen on the Auger spectra for Sc has been reported by Malinowski². Concentrating on the "peak height," in the derivative spectra, of the core-core-valence (CCV) $L_{23}M_{23}V$ signal, Malinowski reported a linear relationship between peak height and deuterium³ content in his scandium deuteride films. His results are somewhat restrictive in terms of their usefulness for surface chemical analyses because he studied only the two component scandium-deuterium (hydrogen) system. In doing this he felt that "in order for AES to be sensitive to these chemical changes (the hydrogen-induced changes in peak height) due to hydriding it is necessary that the Auger transition not only contains a valence electron (the LMV transition on which he concentrated exclusively), but that AES surface is free of contaminants such as oxygen which can form oxides and also change the same valence-associated peak heights."⁴ In the results presented below, all of the Auger signals for scandium will be considered in terms of the total shape changes which hydrogen (deuterium), oxygen and nitrogen, separately, induce.

In our study a catalog of spectra was sought which could possibly be used to "fingerprint" the changes in Sc line shapes in multicomponent, as opposed to two-component, surface systems. The changes observed can be sorted out in terms of Sc-Sc, Sc-H, Sc-O, and Sc-N bonding⁵. The ultimate goal of these fingerprint studies is to be able to decompose the Sc-AES line shapes from a multicomponent Sc-O-H-N system into component signals indicative of separate Sc-Sc, Sc-O, Sc-H, and Sc-N bonding. Such decomposition has been shown to be feasible for the hydrogenated silicon oxynitride system⁶. The component signals presented in this report are to be used in a test of the feasibility of such a decomposition analysis for a multicomponent scandium-compound system.

II. Experimental

Most of the data presented below were obtained using a double-pass cylindrical-mirror-analyzer (CMA) in a commercial (Physical Electronics Model 550) surface analysis system. The CMA was operated in the nonretard mode with Auger data taken in $d[EN(E)]/dE$ form using a 1 volt peak to peak modulation voltage. Core level excitation was provided by a 3-keV electron beam from a gun coaxial with the CMA. The primary beam current was 1 μ A. The experimental system was computer (Digital PDP-11/04) controlled during data acquisition. This experimental system was also equipped to perform X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) measurements on the samples. Such measurements, as well as low-resolution electron energy loss measurements, were made on a number of the samples but only a limited amount of the XPS data will be presented, for comparisons, below. A differentially pumped ion gun was used both for SIMS and for ion-sputter cleaning of the surfaces of our samples. Surface cleaning was performed in this system with 4.5-keV argon ions.

All of our scandium samples started with thin, elemental Sc films deposited ~500 nm thick onto molybdenum or sapphire substrates using electron beam evaporation. The substrates were held at 400°C during deposition. Scandium dideuteride was formed in situ by exposing a freshly deposited Sc film to a 1330 Pa (10 torr) atmosphere of deuterium for one hour with the substrate at 400°C, then cooling the deuterided film to room temperature in the presence of the deuterium gas. The scandium deuteride films used in our investigations had a 1.9 loading ratio. Alternatively, scandium oxide was formed in situ by exposing a Sc film to 99.99 percent pure oxygen at 66 Pa (0.5 torr), with a sample substrate temperature of 600°C, for one hour in the sample preparation chamber of the experimental system. SIMS was used to check the bulk composition of the films after deposition.

In a check for the possible influence of instrumental artifacts on the Auger data, some measurements were also made using a single-pass CMA (a modified Physical Electronics Model 545) system. The samples used with this system were the elemental Sc films described above, which were initially contaminated with surface oxygen and carbon resulting from the transfer in air between the deposition system and this second Auger system. Ion bombardment cleaning of the samples in this second system was done with 2-keV neon ions. With this system, attempts at loading cleaned Sc films with deuterium by ion implantation always resulted in a significant nitrogen contamination. Thus a study of the effects of nitrogen on the Sc line shapes was made in this system by intentionally implanting cleaned elemental Sc films with nitrogen. Except for the very low, 0 to 15 eV, energy region of the spectrum, and for the absence of the 215-eV argon signal in the data taken with the second system, the elemental Sc spectra taken with the two systems were identical. Thus only the nitrogen-implanted Sc data taken with the second system will be presented below. Both systems had base pressures of approximately 2×10^{-8} Pa ($\sim 1 \times 10^{-10}$ torr).

III. Results and Discussion

The first derivative, $d[EN(E)]/dE$, AES survey scans (0 to 550 eV) for elemental Sc, Sc-D, and Sc-O are shown in Figure 1 while similar scans for elemental Sc and Sc-N are shown in Figure 2. Although some of the details of the bonding-induced changes in the Sc Auger line shapes are not evident in the resolution presented in these spectra, gross changes in features are seen, as between the elemental Sc and the Sc-O or Sc-N data. What should be noted in these figures, however, are the low levels of oxygen and carbon impurities on the elemental Sc and Sc-D surfaces. As shown here it is possible to reduce these impurity signals to the point where they were no longer evident in the spectra. This was important in defining the small hydrogen-induced changes in the Sc line shapes because these changes could be easily masked by changes induced by small amounts of oxygen contamination. Using published sensitivity factors⁷ AES estimates of the surface contaminants on either the elemental Sc or the Sc-D samples were found from the spectra in Figure 1 to be less than 1 at.% for both oxygen and carbon. Such Auger estimates of surface quantities for the data in Figures 1 and 2 gave a Sc/O ratio of -0.8 for the Sc-O surface and also -0.8 for the Sc/N ratio on the Sc-N surface. These ratios are to be compared with the ratios for the corresponding known (bulk) binary Sc compounds⁸: 0.67 for the oxide; and 1.0 for the nitride, respectively.

From Figures 1 and 2 one sees that the Sc Auger signals can be separated into two groupings according to energy (as can the Auger signals from any 3d metal). In contrast to the low energy group, the high energy group is seen to be very rich in line shape structure. This is due to the fact that this energy region contains signals from numerous Auger transitions, core-core-core (CCC), CCV and core-valence-valence (CVV). The high energy Sc spectra from Figures 1 and 2 are replotted in expanded form in Figures 3 and 4. In order to identify the features in such spectra one turns to tabulations of calculated energy levels for the material in question and of the calculated energies for allowed Auger transitions. Tentative assignments for the features in the derivative spectra of Figure 3 for the elemental Sc, the Sc-O and the Sc-N surface systems are given in Table 1. The catalog of Auger energies of Coghlan and Clausing³ was used in making these assignments. Uncertainties in these assignments come primarily from the fact that the tabulated energies were calculated using an atomic model and hence solid state effects on the energy level distributions as well as on the initial and final state response of the surface systems to the presence of one, and then two holes are not taken into account. Secondly, the calculated energies are for elemental Sc and not for the compound. Integrations of the elemental Sc and the Sc-O spectra in Figure 3 are shown in Figure 5. These spectra are in reasonable agreement in shapes and energy positions with integral XPS data taken on these same samples, also plotted in Figure 5, and with published XPS results of de Boer et al.¹⁰. The tentative assignments of Table 1 are also in rough agreement with those given by de Boer et al. Core-level XPS measurements and related electron-excited ionization loss measurements were also made on our samples to aid in making the assignments of Table 1.

From the spectra in Figures 3 and 4 one sees that the interaction of oxygen or nitrogen with Sc brings about large changes in the Sc signals in this high energy region of the spectrum. For oxygen these changes are traceable to changes in the core-level energies for Sc, to changes in the features related to plasmon and other characteristic losses and, for the CCV and CVV signals, to changes in the valence electron distributions. For the Sc-N spectra, the changes in the spectra in this region are further complicated by the fact that the N-XVV signal and its associated loss structure are superimposed on part of the Sc signals. Although this would add to the difficulties in interpreting the spectra in terms of Auger transitions, for fingerprinting purposes this overlap is of less importance and the Sc-O and Sc-N spectra may be taken as clearly representing these two types of surface chemical bonding on Sc.

The Sc spectral changes in Figure 3 induced by hydrogen are weaker than those which result from oxygen and nitrogen but they are measurable. The hydrogen-induced changes are not in good agreement with those on which Malinowski concentrated in his study [2] of the ScD_2 system. Our results for the Sc-O system suggest that some of the hydrogen induced changes in Malinowski's study may have been masked by the effects of a small surface oxygen contamination. Considering our results for the hydrogenated silicon oxynitride system [6], it would seem that the hydrogen induced changes of Figure 3 are sufficiently clear for fingerprint use in a signal decomposition processing of data from the multicomponent Sc-compound system.

In Figures 6 and 7 the low energy, derivative Sc signals from Figures 1 and 2 are replotted in expanded form. According to the Coghlan-Clausing calculations [9] one would expect the CCC signals $L_1L_{23}M_{23}$ to be the strongest in this energy region with the $M_{23}VV$ signals the next strongest. In order to sort out the contributions of these two groups of transitions to the observed signal structure, measurements of the signals in this region were made with primary beam energies of 500 and 250 eV in order to turn off the L_1 core hole channel and then all L core hole decay channels, respectively. These data are shown in Figure 8 for the elemental Sc surface. The measured spectra were found to be nearly identical for all three primary beam energies indicating that the observed signals are not initiated through L shell levels. The absence of strong $L_1L_{23}M_{23}$ signals is probably due to the short L_1 core hole lifetime resulting from the allowable $L_1L_{23}M_{23}$ and $L_1L_{23}V$ Coster-Kronig transitions.

Other non Auger decay related sources of secondary electron structure in this low energy region which should be considered as possible origins of the observed signals include the excitation of characteristic loss features and the generation of diffraction related structure. Characteristic loss structures can be ruled out because, as noted above, the signal structure was found to be independent of primary beam energy between 250 eV and 3 keV. Diffraction related structure at low energies is found¹¹ to be sensitive to the angle of incidence of the primary beam with respect to the sample surface. Since the data taken on the two experimental systems used in this study involve differences in this angle of incidence yet show essentially the same signal structure for data at energies greater than -15 eV, the features in Figures 6 and 7 above 15 eV are not related to such diffraction processes. This is also true when these signals are compared with the peaks reported by McDonnell et al.¹² as occurring from the diffraction of emitted secondary electrons. Besides the fact that the features considered by McDonnell et al. occur above 100 eV, the signals in Figures 6 and 7 do not have the right shapes to be identified with such diffraction features.

From these considerations one is led to the conclusion that the low energy features seen in Figures 6 and 7, at least for energies greater than -15 eV, are signals related to Auger transitions, and most probably the $M_{23}VV$ processes. One sees that the shapes of these signals are affected by chemical bonding changes with even hydrogen-induced changes in line shape visible in Figure 6. These signals can therefore also serve as chemical bonding fingerprints in an analysis of Sc surface compounds.

IV. Summary and Conclusions

A catalog of Sc Auger signals representing elemental Sc, Sc-O, Sc-N and Sc-H bonding have been measured and presented in derivative form. Features in the Auger line shapes characteristic of the different types of bonding are seen in these data and this catalog should thus be appropriate for a future test of the idea that the AES Sc signals from the multicomponent compound system can be treated as the simple superposition of the component curves presented here. The Sc data are found in two energy regions and changes in line shape for the signals in either region should be sufficiently indicative of surface chemical changes for such a test.

Identification of the sources of the Auger signals in terms of various CCC, CCV and CVV transitions shows that those signals in the low energy region are related only to MVV transitions while those in the high energy region are initiated through L shell excitations. Although the spectra in the high energy region, the only region for which data are readily available in XPS, are rich in line shape structure the signals involving only core levels are stronger than those which involve valence electrons. The data in this region are thus poor in VB information. Despite this fact, chemical bonding changes result in clearly observable changes in Auger line shapes in both the high and the low energy regions of the Sc spectra. Measurements of the nonmetal Auger spectra in the binary compounds may also be useful for chemical analysis.

ACKNOWLEDGEMENTS

The authors would like to thank J. Lyn Provo, General Electric Company, Neutron Devices Department, for sample preparation.

REFERENCES

1. R. Wiswall in "Hydrogen in Metals II, Application-Oriented Properties," G. Alefeld and J. Volkl, eds. (Springer-Verlag, New York, 1978), p 201.
2. M. E. Malinowski, J. Vac. Sci. Technol. 19, 120 (1981).
3. Note that deuterium is frequently substituted for hydrogen in studies of hydride systems because the substitution should make no significant difference in the electronic energy level structure of the compounds, while the use of deuterium in making the compounds avoids complications in related mass spectroscopy measurements that may result from the presence of hydrogen containing contaminants in the experimental system.
4. M. E. Malinowski, J. Less-Common Metals, 89, 1 (1983).
5. Carbon is also a common surface contaminant and the possibility of a scandium carbide forming on our surfaces could not be ignored. Because of its position in the periodic table, however, scandium would be expected to form carbides with properties characteristic of other rare-earth carbides. These are known to be susceptible to chemical attack by ambient gases, readily decomposing in moist air (see e.g., T. Ya. Kosolapova, G. N. Makarenko and L. T. Domasevich, in Studies in Soviet Science: REFRACTORY CARBIDES, G. V. Sasonov, ed. (Consultants Bureau, New York, 1974) pp 417-422). Despite the expected unstableness of scandium carbides on the surface, attempts were made to make a pure scandium carbide to provide fingerprint carbide spectra for this study. So far these attempts have been unsuccessful so data indicative of Sc-C bonding could not be included in this report.
6. H. H. Madden and G. C. Nelson, Appl. Surf. Sci. 11/12, 408 (1982).
7. Handbook of Auger Electron Spectroscopy, L. E. Davis et al., eds. (Physical Electronics Division, Perkin-Elmer, Eden Prairie, MN 1976), p 13.
8. Scandium: Its Occurrence, Chemistry, Physics, Metallurgy, Biology and Technology, C. T. Horovitz, ed. (Academic Press, London, 1975), pp 154-172.

9. W. A. Coghlan and R. E. Clausing, Atomic Data 5, 317 (1973).
10. D. K. G. de Boer, C. Haas and G. A. Sawatzky, J. Phys. F: Met. Phys. 14, 2769 (1984).
11. H. H. Madden, J. Vac. Sci. Technol. A2, 961 (1984).
12. L. McDonnell, B. D. Powell and D. P. Woodruff, Surf. Sci. 40, 669 (1973).

FIGURE CAPTIONS

- Figure 1. Derivative (survey) Auger spectra from elemental scandium, scandium-deuteride and scandium-oxide.
- Figure 2. Derivative (survey) Auger spectra from elemental scandium and from scandium-nitride.
- Figure 3. Derivative, high-energy Sc Auger signals from elemental scandium, scandium-deuteride and scandium-oxide.
- Figure 4. Derivative, high-energy Sc Auger signals from elemental scandium and from scandium-nitride.
- Figure 5. Integral, high-energy Auger signals from Sc in elemental scandium (upper two curves) and in scandium-oxide (lower two curves) produced by X-ray excitation and by electron beam excitation. (Curve not yet available.)
- Figure 6. Derivative, low-energy Sc Auger signals from elemental scandium, scandium-deuteride, and scandium-oxide.
- Figure 7. Derivative, low-energy Sc Auger signals from elemental scandium and from scandium-nitride.
- Figure 8. Derivative, low-energy Sc Auger signals from elemental scandium excited with primary electron beams of energies 3 keV, 500 eV and 250 eV.

TABLE Ia: Identification of Observed Auger and Associated Loss Peaks from Elemental Scandium

<u>Derivative*</u> (eV)	<u>Integral</u> (eV)	<u>Designation</u>
289.4	289.0	$L_3M_1M_1$ and $L_2M_{23}M_{23}$ M_1 Core Loss
297.6	295.0	$L_2M_1M_1$
309.2	309.2	$L_3M_1M_{23}$ and $L_2M_{23}M_{23}$ M_{23} Core Loss
318.4	317.8	$L_3M_1M_{23}$ and $L_2M_{23}M_{23}$ 2nd Plasma Loss
329.8	329.4	$L_2M_{23}M_{23}$ 1st Plasma Loss
336.0	334.0	$L_3M_{23}M_{23}$ and $L_3M_{23}V$ M_{23} Core Loss
340.0	338.2	$L_2M_{23}M_{23}$ and $L_3M_{23}V$ 2nd Plasma Loss
344.2	342.8	L_3M_1V
351.6	349.0	$L_3M_{23}V$ 1st Plasma Loss
361.4	360.0	$L_3M_{23}V$ Valence Electron Loss or Oxide $L_3M_{23}V$
367.0	365.4	$L_3M_{23}V$
370.6	369.8	$L_2M_{23}V$
395.2	394.2	L_3VV
401.4	400.8	L_2VV

*Derivative energy measured at peak's high energy minimum

TABLE Ib: Identification of Observed Auger and Associated Loss Peaks from Scandium Dideuteride

<u>Derivative*</u> (eV)	<u>Integral</u> (eV)	<u>Designation</u>
289.0	288.2	$L_3M_1M_1$ and $L_2M_{23}M_{23}$ M_1 Core Loss
297.6	295.2	$L_2M_1M_1$
309.2	309.0	$L_3M_1M_{23}$ and $L_2M_{23}M_{23}$ M_{23} Core Loss
318.4	317.2	$L_2M_1M_{23}$ and $L_2M_{23}M_{23}$ 2nd Plasma Loss
329.8	329.4	$L_2M_{23}M_{23}$ 1st Plasma Loss
335.0	333.4	$L_3M_{23}M_{23}$ and $L_3M_{23}V$ M_{23} Core Loss
339.2	337.6	$L_2M_{23}M_{23}$ and $L_3M_{23}V$ 2nd Plasma Loss
344.2	342.6	L_3M_1V
351.6	349.0	$L_3M_{23}V$ 1st Plasma Loss
361.4	360.0	$L_3M_{23}V$ Valence Electron Loss or Oxide $L_3M_{23}V$
366.6	365.0	$L_3M_{23}V$
370.6	370.0	$L_2M_{23}V$
395.2	394.2	L_3VV
400.2	400.0	L_2VV

*Derivative energy measured at peak's high energy minimum

TABLE Ic: Identification of Observed Auger and Associated Loss Peaks from Scandium Oxide

<u>Derivative*</u> (eV)	<u>Integral</u> (eV)	<u>Designation</u>
291.6	290.4	$L_3M_1M_1$
304.8	304.4	$L_3M_1M_{23}$
311.8	311.0	$L_2M_1M_{23}$
320.0	318.0	$L_{23}M_{23}M_{23}$ First Plasma Loss
333.8	330.2	$L_{23}M_{23}M_{23}$
343.4	342.6	$L_3M_{23}V$ First Plasma Loss
359.2	357.4	$L_3<_{23}V$
365.6	363.4	$L_2M_{23}V$
392.0	390.4	L_3VV
398.2	397.6	L_2VV

*Derivative energy measured at peak's high energy minimum

$\frac{dN(E)}{dE}$