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D. M. Zehner and H. H. Madden

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HIGH RESOLUTION LMM AUGER SPECTRA FROM ARGON IMPLANTED IN Be AND Si*

D. M. Zehner
Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

and

H. H. Madden
Sandia Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

The $L_{2,3}M_{2,3}M_{2,3}$ and $L_{2,3}M_{1}M_{2,3}$ Auger electron spectra from argon implanted by 1 KeV ion bombardment in Be and Si crystals, have been obtained using a double pass CMA operated in both the non-retard and retard modes. Background subtraction and loss-deconvolution were subsequently applied to obtain the final results. The argon-in-Be spectrum consists of a series of narrow peaks (FWHM less than 2 eV) which are sharper than those previously reported for the $L_{2,3}M_{2,3}M_{2,3}$ spectrum from solid argon. Associating the major peak in our spectrum with the $L_{3}M_{2,3}M_{2,3}(^1D_2)$ peak in the gas phase spectrum leads to an identification in terms of energy separations of our peak structure with the principal peaks of the gas-phase spectrum to within 0.5 eV. We conclude that the transitions responsible for the Auger spectrum can be characterized as quasiautomic, although the multitude of gas-phase satellite peaks is not seen in our results. Peaks in the argon-in-Si spectrum are slightly broader than those in the argon-in-Be spectrum. As a result of screening by the conduction electrons in the host material, our argon Auger emission energies are higher than those in the gas-phase spectrum.

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I. INTRODUCTION

The technique of Auger electron spectroscopy (AES) has progressed significantly since its initial application by Lander¹ in 1953 to the identification of the atomic constituents present in the surface region of a solid. In particular, information specific to the valence band electronic structure has been obtained from analysis of the electron energy distributions of Auger transitions involving one or more valence electrons and the subsequent comparison with results of model calculations.² Moreover, for atoms adsorbed on or embedded in a material, information about their local environment and thus the extent of interaction with the host can also be acquired from similar analysis and treatment of Auger spectra. In order to obtain this type of information, the true lineshape of the Auger transition of interest must be determined. The development and application of background removal⁴ and loss-deconvolution⁵ techniques provide for the elimination of distorting effects and make possible the acquisition of such lineshapes.

Auger transitions from atoms in solids involving one or more valence band electrons have generally been classified as being band-like (lineshape energy widths directly correlated with the density of states (DOS) of the material) or quasiautomic (lineshape is controlled by final-state effects generally resulting in peaks with narrow energy widths). Derivative, $dN(E)/dE$, data have been used frequently in making such assignments as well as comparison to gas-phase spectra when available. Subsequent investigations employing lineshape correction techniques and utilizing $N(E)$ data have confirmed the band-like interpretation of spectra obtained from several materials and in select cases provided additional information about matrix elements and surface

effects.² Recently, the application of such techniques to Auger spectra obtained from Cu have revealed both band-like and quasiautomic features, the latter being peaks with full widths at half maximum (FWHM) approximately 2 eV.⁶ The modeling, theory, and interpretation of these data are the subject of several investigations.⁷

The gas-phase Auger spectra of the inert gases (Ne, Ar, Kr and Xe) have been measured previously.⁸ In addition to the principal transitions, a large number of satellite lines are observed which can be assigned to Auger transitions from doubly ionized initial states or to shake-up processes. Auger spectra also have been obtained from solid argon formed by condensation on a metal cold finger at ~ 10 K.⁹ The spectra could be simulated by using broadened gas-phase data, restricted to the principal lines, which lead to a quasiautomic characterization of the transitions from the solid. In addition to the broadening, a coverage dependence of the transition energies was observed and related to environmental effects experienced by atoms situated on top of the metal compared with effects experienced by atoms surrounded by other argon atoms.

Argon ions can be easily embedded in a solid, subsequently becoming neutral implants. An investigation of the Auger spectrum from implanted argon should provide information that can be compared with both gas-phase and condensed spectra and permit an evaluation of environmental effects. In order to provide these data and to examine the suitability of data processing techniques on spectra that are expected to consist of a series of narrow peaks, a study of the $L_{2,3}M_1M_{2,3}$ and $L_{2,3}M_{2,3}M_{2,3}$ transitions from argon-in-Be (Ar/Be) and argon-in-Si (Ar/Si) was initiated. Initial results of this investigation are reported in this article.

II. EXPERIMENTAL PROCEDURES

A polycrystalline Be sample of 5N purity and a Si(111) crystal of 4N purity, both cleaned by Ar ion bombardment and annealing techniques, were used in these investigations. Argon was implanted in the samples at room temperature at an ion energy of 1000 eV using a 5 μ A beam current obtained by operating the ion gun in an argon gas pressure of 4×10^{-3} Pa. Under these conditions, the total dose for each sample was in the 10^{16} to 10^{17} ions/cm² range. Although the lattice locations of a wide variety of implanted atoms in Be and Si are well known,¹⁰ such information is not available for argon implanted in these materials.

The measurements were made in a UHV system containing both ion and cryopumping facilities. With this arrangement, the background gas pressure during data acquisition periods was typically below 10^{-8} Pa. Cryopumping was required to reduce oxygen containing constituents in the background gas and thus minimize their cracking in the presence of the electron beam and the subsequent formation of oxide on the sample surfaces.

All measurements were obtained with a double pass cylindrical-mirror-analyzer (CMA) containing a coaxial electron gun. When operated in the non-retard mode a constant energy resolution of 0.7% was obtained, while in the retard mode the energy resolution was 1.2% of the pass energy, chosen to be 50 eV in these investigations. Derivative, $dN(E)/dE$, data were obtained by using 1.0 and 0.2 V peak-to-peak modulation amplitudes in the non-retard and retard modes, respectively. Signal averaging was used to produce a spectrum with a signal to noise ratio of at least 25.

To obtain the desired lineshape of the spectrum being measured, several distortions in the measured signal must be removed subsequent to the data acquisition. The output signal of the CMA when operated in the non-retard

mode is proportional to $E \times N(E)$ and to $E^{-1.5} \times N(E)$ when operated in the retard mode. Thus all data were corrected for the appropriate energy dependence after initially integrating the $dN(E)/dE$ spectra. The smoothly varying secondary-electron backgrounds in the Auger spectra were then removed using a correction technique described by Sickafus.⁴ Signal distortion due to inelastic losses suffered by some of the Auger electrons in leaving the solid, as well as instrumental broadening, were removed by deconvolution techniques employing a near-elastic backscatter spectrum. The suitability of using these techniques has been discussed previously.⁵

III. RESULTS

Results of measurements made in the non-retard mode and used to obtain the high resolution LMM Auger spectrum of argon implanted in Be are shown in Fig. 1. Auger data following integration and corrections for both a smooth background variation and for the energy dependence of the analyzer are plotted as curve S in this figure. A backscatter spectrum (loss function) taken under the same operating conditions and also corrected for the energy dependence of the analyzer is plotted as curve L in the same figure. The result of ten (van Cittert) deconvolution iterations using functions S and L is given as curve W_{10} in Fig. 1. These data are plotted as a function of energy using the analyzer's energy scale and have not been corrected for the work function of the spectrometer. Measured emissions from the $L_{2,3}M_1M_{2,3}$ and $L_{2,3}M_{2,3}M_{2,3}$ Auger transitions are shown in the 190 to 205 eV and 205 to 225 eV portions of the spectrum, respectively. The assignments of the major peaks in the spectrum are given in Table I along with their measured energies.

For purposes of comparison, the deconvoluted $L_{2,3}M_{2,3}M_{2,3}$ spectrum of Ar/Be obtained in the retard mode is plotted in Fig. 2. Although the energy resolution of the CMA increases by a factor of two in going to the retard mode, a comparison of the data subsequent to deconvolution shows only a slight decrease in the FWHM of the major features. This also holds true for the $L_{2,3}M_{1}M_{2,3}$ spectrum not shown here. Additionally, a comparison of the changes in shape of the spectra in the regions of peaks F and K suggest that they may arise as a consequence of instabilities occurring in the deconvolution process due to a lack of resolution in the analyzer.⁵ The deconvoluted $L_{2,3}M_{2,3}M_{2,3}$ spectrum of argon implanted in Si obtained in the non-retard mode is plotted also in this figure. A comparison of these data with the data for Ar/Be obtained under the same operating conditions indicates that, although all major features are present and occur at approximately the same energies, the individual peaks are broader for Ar/Si. This increased broadening is also observed in the $L_{2,3}M_{1}M_{2,3}$ data not shown here as well as in data obtained in the retard mode.

The $L_{2,3}M_{2,3}M_{2,3}$ data from solid argon, reported by Nuttall and Gallon,⁹ are also plotted in this figure. These data were obtained from condensed argon adsorbed in submonolayer coverages on a Ag substrate at ~10 K and have not been corrected for background or loss related effects. The relative intensities and energy separations of the gas-phase data of Werme et al.¹¹ are represented by the line spectrum also plotted in this figure. Other gas-phase results are in excellent agreement with the data illustrated here. The spectra have been arbitrarily shifted so that the $L_{3}M_{2,3}M_{2,3}(^1D_2)$ component in each are all aligned at the same relative energy.

VI. DISCUSSION

From an examination of the experimental results shown in Fig. 1 and the assignments given in Table 1, it is apparent that all principal lines present in the argon Auger gas-phase data which are expected to be resolved by the analyzer employed in this investigation are observed in the Auger spectrum from Ar/Be. Associating peak J with the $L_2M_{2,3}M_{2,3}(^3P_{0,1,2})$ transition in argon and using it as a reference peak, the measured energy separations for all other peaks in the spectrum for Ar/Be are within 0.5 eV of the energy separations observed in the gas-phase data, and with the exception of peak G, within 0.2 eV. While the significance of the shapes of the deconvoluted spectra near peaks F and K has been questioned previously, from an examination of the data plotted in Fig. 2, it appears that some signal intensity is present in the region of peak K. Molybdenum which could be occasionally detected on the annealed Be surface (Intensity of Mo Auger peak/Intensity of Be Auger peak < 0.005) cannot be identified positively as the source of this signal. Although the gas-phase data exhibit 28 satellite lines within an energy interval appropriate to that shown in Fig. 1, they are not resolved due to their weak intensities and the level of noise present in our measurements. Thus, they are not believed to be responsible for the intensities at peaks F and K or A, which is also unidentified at this time. All principal lines are also observed in the Auger spectrum for Ar/Si but the exact energy separations are more difficult to determine due to the broadening of these lines. However, energy separations within the $L_{2,3}M_{2,3}M_{2,3}$ spectrum are determined to be within 0.5 eV of the gas-phase results.

Previous experience with the data processing used in this investigation suggests that these procedures may affect the relative intensities of narrow peaks within a group, as observed in the spectra presented here. In particular, note the relative heights of peaks H and I for the Ar/Be data in figs. 1 and 2. Thus, it is difficult to compare and to interpret differences between these data and the gas-phase spectrum. Nevertheless, it should be noted that peak G was always observed to be more intense than peak J. This relationship observed in spectra from both Ar/Be and Ar/Si is opposed to that shown in the gas-phase data and may reflect changes caused by the host environment.

In contrast to the 0.2 to 0.3 eV FWHM values determined for the principal lines in the argon gas-phase Auger spectrum,¹¹ the smallest FWHM value for Ar/Be, exhibited in Fig. 2, is 1.3 eV. However, as noted previously, changes in the curves near peaks F and K for data obtained in both operating modes of the analyzer are characteristic of lines which are narrower than the instrument response function used in the deconvolution process. Thus the widths of the principal lines could be considerably smaller than the 1.3 eV value which should be considered an upper limit. Nevertheless, this width is smaller than the 2.0 eV FWHM value determined by Nuttall and Gallon⁹ for the Auger spectrum from condensed argon. Although they did not account for loss related effects in treating their argon data, the FWHM values of the principal lines are determined primarily by the energy resolution of the analyzer. Since their resolution was better than that used in this investigation, this difference in width is significant and may indicate a difference in the processes responsible for the broadening in these two differing solid environments.

Moreover, since the Auger data for Ar/Be and Ar/Si taken in the non-retard mode were treated identically, it can be concluded that there is a difference

in the degree of broadening for embedded argon induced by the host material. Differences in site location or multiple site locations, and thus differing local environments for the embedded argon in the two hosts, could be responsible for some of this difference. The absence of site location information hinders an evaluation of this aspect. From a chemical viewpoint, the electronegativity difference is larger between argon and Si than between argon and Be, and one might expect a stronger interaction which produces the broadening in the Si host when it responds to the initial hole and final two-hole states. Furthermore, since the plasmon energy in Si is somewhat closer to the binding energy of the $M_{2,3}$ level in argon than is the plasmon energy in Be, one might expect a stronger interaction of the argon 3p electrons with the Si host subsequent to the initial hole creation, resulting in additional broadening. However, in both spectra the argon Auger linewidths are much narrower than the DOS widths of the host material, a fact which argues against any interatomic Auger processes.

The energies of the peaks determined in the investigation of Ar/Be and recorded in Table I average 7.6 eV higher than those observed in the gas-phase results. While this increase in emission energy is similar to that measured by Nuttall and Gallon⁹ for submonolayer coverages of condensed argon, it should be noted that a work function correction, due to differences in reference levels, must be applied to our results. This will increase the absolute energy difference between the gas-phase and implanted data. As noted by Nuttall and Gallon⁹ this increase in energy can be attributed to electron screening effects that can occur in the host material but which are not possible in the gas-phase. Since the Auger emission energies determined for Ar/Si are within 0.5 eV of those determined for Ar/Be, the size of the screening effect is comparable in both materials.

V. CONCLUSIONS

Measurements have been made of the Auger spectra of argon embedded in both Be and Si. The spectra consist of a series of narrow peaks identifiable with all principal lines observed in the gas-phase data and this fact permits a quasiautomatic characterization of the Auger transitions from implanted argon. Differences in relative intensities of the principal lines, increased broadening of the individual lines and a shift in emission energies reported for the spectra from implanted argon, as compared with the gas-phase data, are attributed to the solid state environment. The extent of broadening is observed to depend on the host material.

VI. ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. $L_{2,3}M_{1,2,3}$ and $L_{2,3}M_{2,3}M_{2,3}$ spectra from argon implanted in Be. Curve L - loss function used as system response function in deconvolution. Curve S - AES signal after correction for analyzer energy dependence and secondary-electron background but before deconvolution. Curve W_{10} - the result of ten (van Cittert) deconvolution iterations using curves L and S. Peak labels correspond to atomic model peak locations (Table I). Zero levels for curves are set on the right-hand side of each curve.

Figure 2. $L_{2,3}M_{2,3}M_{2,3}$ spectra from argon: (a) line diagram of gas phase results, (b) implanted in Be and obtained in retard mode, (c) implanted in Si and obtained in non-retard mode, (d) condensed on Ag substrate at ~ 10 K. Zero levels for curves are set on the right-hand side of each curve.

TABLE 1. Experimental Values of $L_{2,3}M_{1,2,3}$ and $L_{2,3}M_{2,3}M_{2,3}$ Peaks and Peak Separations (eV)

Peak Label	Assignment	Experimental Energy		ΔE Separations from $L_{3,2,3}M_{2,3}(^3P_{0,1,2})$	
		Gas Phase ^a	Implanted in Be ^b	Gas Phase	Implanted in Be
B	$L_{3,2,3}M_{2,3}(^1P_1)$	187.33	195.0 $\pm$ 0.2	19.90	19.7
C	$L_{2,3}M_{1,2,3}(^1P_1)$	189.49	197.0	17.74	17.7
D	$L_{3,2,3}M_{2,3}(^3P_2)$	191.13	198.8	16.10	15.9
E	$L_{2,3}M_{1,2,3}(^3P_2)$	193.13	200.7	14.10	14.0
G	$L_{3,2,3}M_{2,3}(^1S_0)$	201.09	209.0	6.14	5.7
	$L_{2,3}M_{2,3}M_{2,3}(^1S_0)$	203.23	-----	4.00	---
H	$L_{3,2,3}M_{2,3}(^1D_2)$	203.47	211.0	3.76	3.7
I	$L_{3,2,3}M_{2,3}(^3P_{0,1,2})$	205.21	212.8	2.02	1.9
J	$L_{2,3}M_{2,3}M_{2,3}(^1D_2)$	205.62	-----	1.61	---
	$L_{2,3}M_{2,3}M_{2,3}(^3P_{0,1,2})$	207.23	214.7	← Reference Peak →	

^aWerme et al. (Ref. 11).

^bUncorrected for spectrometer work function.

Treatment of Data Obtained in Nonretard Mode for Ar/Be.

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Comparison of Line Widths for Argon
in Different Environments.