Accuracy of Carbide Analysis Using Auger Electron Spectroscopy

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Quantitative analysis using Auger electron spectroscopy (AES) is most commonly performed using sensitivity factors derived from pure elements. The accuracy of the technique can be quite good for specimens such as stainless steels where many of the elements have adjacent atomic numbers and similar densities. In other situations the analysis can have errors that are greater than 100% of the accepted true value. The reasons for this will be discussed and different methods will be compared for their effectiveness.

INTRODUCTION

Accuracy, the difference between the accepted true value and the result of an analysis, with Auger electron spectroscopy (AES) has seen very slow improvements. There have been relatively very few technical papers addressing this important subject, although there are documents in progress within the International Standards Organization (ISO TC-201 on Surface Chemical Analysis) addressing this subject. By contrast, analysis with the electron probe micro analyzer (EPMA) developed very quickly to the point where a typical accuracy, in the range of a few percent on a relative basis, is commonly reached.

EPMA computer programs for converting x-ray intensities to concentrations follow the ZAF corrections (where Z is atomic number correction, A the absorbance correction, and F the fluorescence correction) are available both in the public domain as well as from all the manufacturers of x-ray spectroscopic equipment. For AES there are no commercially available programs beyond the simple sensitivity factor[1] approach.

This work evaluates the current matrix effect corrections approaches[2, 3] to that using elemental sensitivity factors from measurements with carbide compounds. Sensitivity factors for several experimentally collected stoichiometric metal carbides are compared with those calculated from pure element sensitivity factors using matrix effect corrections.

DISCUSSION

Metal carbides are very important commercial materials, which are utilized for their hardness in cutting tools, for wear-resistant films and semi-conducting films, for diffusion barriers in both silicon and III-V device technology, and as forming carbide-derived carbon (CDC) coatings. This study evaluates the accuracy attainable with stoichiometric carbides from silicon, titanium, zirconium, molybdenum, tantalum, zirconium, and hafnium in AES analysis.

These carbides were obtained as hot isostatically pressed materials and fabricated into 3 mm ϕ discs by ½ mm thick after being ground flat and polished to a scratch free surface. The final polish was a 1 μm diamond abrasive. A flat surface is important since local surface angle changes have dramatic effects on the Auger electron emission intensity. These carbides cannot be pressed void free, to theoretical density, due to cracking problems. One must be careful to check that the materials are homogenous. Specifically, the Mo_2C we analyzed contained unreacted pure Mo grains along with the carbides. With the electron beam image and Si(Li) x-ray detection it is straightforward to select an appropriate area for analysis. It is also important to insure there are no significant microcrystalline orientation effects which might significantly alter the Auger emission intensity. However, this was not done for these specimens.

The electron beam conditions used for specimen excitation must not cause degradation of the standard or unknown. The specimens must be ion sputter cleaned to re-

move adventitious carbon and surface oxides. When sputtering multi element specimens a change in the equilibrium surface composition of the sample may occur[4, 5]. This is known as preferential sputtering as the effect of changing the surface composition within the depth of analysis for the AES signal and data obtained from such specimens will have significant errors. If both the unknown and reference samples have similar preferential sputtering effects, then this source of uncertainty in measurement of the composition of the unknown sample will be self compensated, as was seen with hot-pressed, powdered, and clear single crystal silicon carbide[6]. The change in sensitivity factors between the fractured single crystal SiC and that after ion sputtering was almost a factor of 2 (where the carbon peak greatly increasing relative to the Si Auger peaks). Some data may be available[7] for preferential sputtering of the other carbides so the magnitude of the error in analyzing sputtered materials presented here cannot be estimated.

In the best of all worlds, sensitivity factors for the carbides should be measured after vacuum fracturing and before the surface is contaminated from the residual background gasses in the ultra high vacuum system. Even if that was accomplished determining the local geometry between the electron beam and specimen surface would be very difficult since the fracture surfaces will most likely be irregular, and the geometry must be known. Sensitivity factors for pure elements (and for some compounds where the pure element is not appropriate for analysis, i.e. Na and Cl) are published by the respective AES instrument manufacturers. Such an example is given in this reference by Sekine, et al[8]. Reliable measurements are difficult to make and change with many parameters including a particular analyzer model, electron beam energy, analyzer resolution, eV/step, and peak intensity measurement schemes. In addition, the factors change as electron multipliers age and the spectrometer contaminates. So, it not surprising that only representative tables are provided. Factors must be measured on an individual instrument in close time proximity to the experimental data. A great help here is to measure the spectrometer transfer function and energy calibration[9] using spectra from gold and copper. The output of the referenced computer program is a five page certificate of traceability for the spectrometer being measured.

To determine the pure element sensitivity factors, high purity (99.999%) element standards[10] (the carbides were also from the same source) were prepared similarly to the carbides mentioned previously. As is common practice for AES, all the measured intensities were referenced to pure Ag. The pure element standards, carbides and the Ag were placed in a SS304 holder and kept under vacuum. Likewise, sensitivity factors for the carbides were determined under identical measurement conditions for all the data. For example, the instrumental configuration including sample orientation to the electron beam and spectrometer, specimen tilt angle, and excitation conditions must be constant. For an excellent general discussion see[11].

Particular attention shall be given to the data collection following parameters. The energy resolution affects peak shapes. With carbides the spectrum is rich in high frequency information, which is easily affected by the analyzer resolution settings. Unless peak areas are used to measure the signal intensities, the energy resolution of the electron energy analyzer (that is determined by choice of aperture sizes and pass energy or retardation ratio) will be the same for the unknown-sample measurement as for the measurement used to generate the sensitivity factors[12]. The magnitude of the energy step (eV per channel) used to acquire spectral data must be adequate for the given resolution to properly sample the peak. The spectral scan rate shall be kept constant since this affects the total number of electron detected per unit time. If data is collected in the integral mode and differential spectra are analyzed the mathematical process shall be similarly repeated. Likewise, if energy modulation is used, it shall be applied consistently to the entire data set. It is also important that the electron detector gain be stable and linear. If analog detection is used the same time constant shall be applied. For pulse counting systems the detector voltage shall be adjusted properly so the signal intensity is proportional to electron beam current and that appropriate dead time corrections are applied to the data.

The measurement of background intensity in the integral spectra is difficult since the background has a significant slope. Often the net intensity is measured by subtracting the background on the high energy side of the peak or drawing a sloped background under the peak. However, this procedure is not rigorous since the background is not linear. Another approach involves differentiating the integral spectra and measuring the resultant peak-to-

peak amplitude. However, the carbon peak shape changes for the different carbides, as does the metal peaks themselves. An alternate approach involves integrating the differential spectra over the energy range of the Auger peaks. This effectively removes the low frequency background and allows for peak shape changes[13, 14].

The simplest quantitative analysis approach, with pure element sensitivity factors[1], described by the following equation, where X_i^{unk} is the atomic concentration for unknown element *i*, and I_i^{RSF} is the pure element sensitivity factor for element I (this is determined from the intensity ratio between that for element *i* and that from silver. The atomic concentration is determined from:

$$X_i^{unk} = \frac{\left(\frac{I_i^{unk}}{I_i^{RSF}}\right)}{\sum_{i=1}^{n}\left(\frac{I_i^{unk}}{I_i^{RSF}}\right)} \qquad (1)$$

This equation, as well as the others, can be used for integral, differential or integrated differential spectra as long as the procedure is used consistently between the standards and unknowns. Errors using this correction technique can be up to one hundred percent[3].

This error can be dramatically reduced to the level of uncertainty in the data collection and reduction procedures by determining sensitivity factors from compound standards that are a match for the unknown specimen. The elemental relative sensitivity factor I_i^{Ec} for the element *i* in a specified compound can be obtained from measurements of I_i^{ref} for the selected element in that compound and of I_{Ag}:

$$I_i^{Ec} = \frac{I_i^{ref}}{X_i^{ref} I_{Ag}} \qquad (2)$$

where X_i^{ref} is the atomic fraction of the element *i* in the compound.

The mathematical corrections[15] for the carbides come from the following equation:

$$I_i^{Av} = \left(\frac{N_{av} Q_{av} (1 + r_{av}) \lambda_{av}}{N_i Q_i (1 + r_i) \lambda_i}\right) I_i^{E} \qquad (3)$$

where the terms N_{av}, Q_{av}, r_{av}, and λ_{av} are the atomic density, the elastic-scattering correction, the backscattering factor, and the inelastic mean free path for a hypothetical average matrix.

The expected result of this equation is to predict the change in magnitude of the sensitivity factor from that of the pure element. For a given carbide this calculated number is applied independently to how the Auger peak intensities are measured. If it is predicted that the direct $E^*n(E)$ spectra increase by 50% the corresponding change should also occur with the dN/dE spectra, whether it is collected or calculated. This should also extend to the integrated dN/dE spectra, as well.

When analyzing specimen stoichiometry it is the ratio of the sensitivity factors used, and not their absolute magnitude, that is important. Consider, for example, using equation (1) with sensitivity factors determined from a reference carbide, using equation (2). If the magnitude of the sensitivity factors increases by any factor for both, the resultant concentrations will not change.

EXPERIMENTAL DETAILS

The pure element and carbide standards were analyzed in a JEOL[16] JAMP-7800 Auger Probe Micro- analyzer. The LaB6 electron source was operated at 10 keV and the incident (Faraday) current was kept at 50 nA at normal incidence. The excitation area on the specimen was either scanned over a 33 μm^2 area for the uniform specimens, or with the electron beam stationary over a few mm^2 area for those carbides where either the porosity or microstructure dictated. The hemispherical electron energy analyzer (using 7 electron multipliers) was operated at 0.4 % resolution in the CRR (constant retarding ratio) mode producing $E^*n(E)$ spectra. The electron emission angle was 60°. Data was collected using a 0.75 eV/channel energy increment with a dwell time of 50 ms averaged over 4 sweeps. The specimens were ion sputter cleaned the specimen was accomplished with the JEOL MIED IV ion gun using 1 kV argon ions until the spectrum was free of surface contamination (mostly oxygen). The specimen was continuously rotated during sputtering to prevent surface roughness[17].

Data collection was controlled by the JEOL "Auger Master" version 3.20 software. The data was exported using the VAMAS[18] protocol and imported in Auger-II[19] data reduction program. Spectral peak intensities were measured using three different techniques:

1. Peak – background (single channel intensities representing the maxima and minima over the selected energy range.

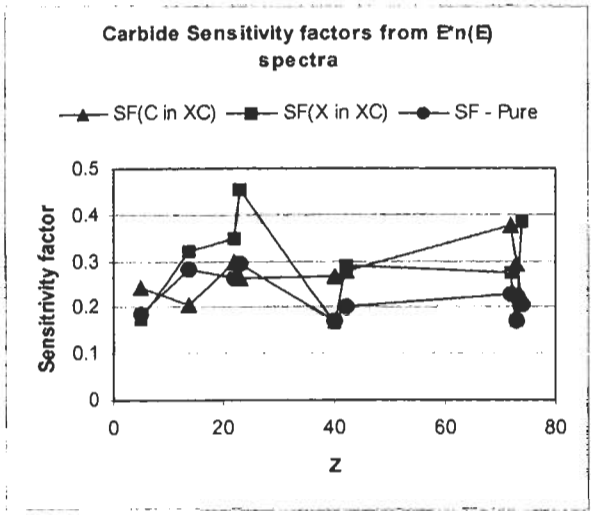

Fig. 1. Carbide sensitivity factors from $E^*n(E)$ spectra

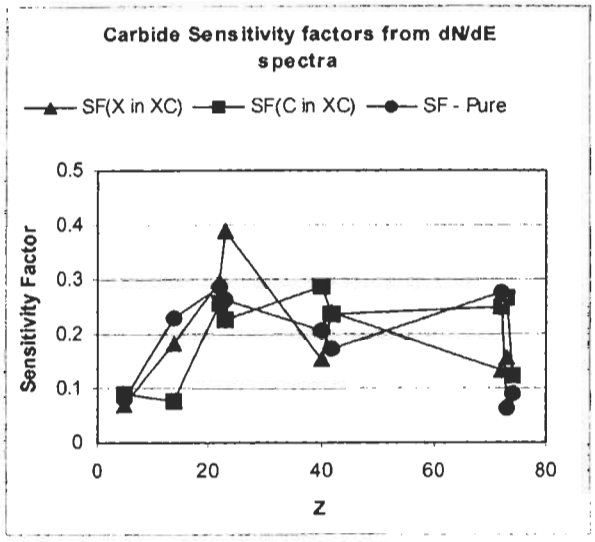

Fig. 2. Carbide sensitivity factors from dN/dE spectra

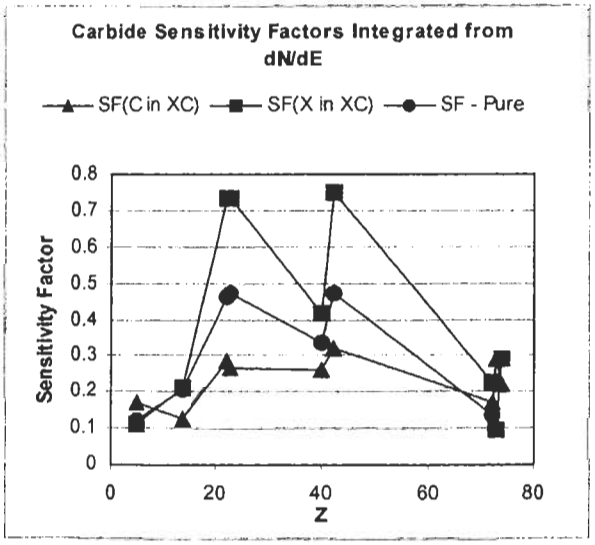

Fig. 3. Carbide sensitivity factors from integrated dN/dE spectra

2. After mathematically differentiating the $E^*n(E)$ spectra the peak - peak heights were measured.

3. The absolute intensities from #2, above, were integrated. This technique represents an approach to remove the slowly varying background seen under the $E^*n(E)$ spectral peak.

RESULTS

Experimental sensitivity factors are plotted in Figs. 1, 2 and 3, respectively, for the $E^*n(E)$, dN/dE, and integrated from the dN/dE spectra. SF is the sensitivity factor X (the metal) in the XC (metal carbide) as a function of Z (atomic number). The sensitivity factors for each pure metal (B, Si, Ti, Zr, Mo, Ta, W, Hf, and Ta) are also plotted. As previously mentioned, there is no correction in the data for preferential sputtering, which is known to have a large effect. These are the factors which, when applied to the measured intensities (using equation 2, results in the proper atomic concentrations reflecting stoichiometric carbide compositions.

One would expect to see different sensitivity factors from those of the pure elements. The dramatic deviation between the different data reduction techniques certainly needs explanation beyond those due to peak shape changes. This is left for further work.

Calculations using the AMSF for the carbides were made using equation 3. Figure 4 compares those sensitivity factors (which are multiplied by the pure element SF), with the pure element SF and the SF for X in XC.

There are several assumptions made using these calculations which can have large effects on the result. One of them is the band gap energy, which changes from the localized specimen temperature. This is a function of the electron beam current density and the thermal conductivity. There are many band gap measurements available to choose from depending upon the specimen structure (which will probably be unknown).

CONCLUSION

To achieve the highest accuracy in quantitative Auger analysis for metal carbides one should use well characterized carbide reference materials as standards for the generation of sensitivity factors. If those materials are not available the errors, even with the most rigorous modeling corrections available, may be several hundred percent. The modeling corrections must include the effect of preferential sputtering.

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