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ELECTRON MICROPROBE ANALYSIS OF
TANTALUM-NITRIDE THIN FILMS

By D. L. Stoltz and J. P. Starkey

Published June 1979

Topical Report

MASTER

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Quantitative chemical analysis of 500- and 2000-angstrom tantalum-nitride films on glass substrates has been accomplished using an electron microprobe X-ray analyzer. In order to achieve this analysis, modifications to the microprobe were necessary. A description of the calibration procedure, the method of analysis, and the quantitative results are discussed.

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SUMMARY

A method was developed for using the electron microprobe for quantitative elemental analysis of tantalum-nitride thin films. Tantalum and nitrogen contents were measured in 500- and 2000-angstrom films deposited on glass substrates. The developed method provides a means to monitor the reactive sputtering process used in the production of hybrid microcircuits.

Before the analysis, it was necessary to modify and calibrate the high voltage power supply on the microprobe in order to improve the stability of its electron beam. A digital voltmeter was installed and calibrated to provide precise control of accelerating potential. During calibration, the response of the tantalum M-alpha characteristic X-rays to low accelerating potentials (less than 4 kilovolts) was measured using 500- and 2000-angstrom tantalum nitride films and a 25-micrometer-thick high purity tantalum standard. Quantitative measurements of the electron beam diameter and depth of penetration in the films were made as a function of the accelerating potential. The resulting total count and peak-to-background ratios showed that a minimum accelerating potential of 2.85 kilovolts was required to produce consistent tantalum M-alpha data.

DISCUSSION

SCOPE AND PURPOSE

This work was done to develop methods for quantitative elemental analysis of tantalum-nitride thin films using the electron microprobe. This type of analysis was needed to support new analytical techniques for hybrid microcircuits and to provide close support for hybrid microcircuit manufacturing. The scope of this endeavor includes a description of the necessary equipment, a description of modifications to equipment, and calibration procedures for obtaining the necessary data. In addition, the response of the tantalum M-alpha characteristic X-rays to accelerating potentials of less than 4 kilovolts was measured for 500- and 2000-angstrom (50 and 200 nanometers) tantalum-nitride thin films. Electron microprobe measurements of high purity tantalum foil and tantalum-nitride films were used as input to the computer program for quantitative elemental analysis.¹

ACTIVITY

Modifications to Equipment

Initial electron microprobe analyses (EPA) of 500-angstrom thin films were conducted at accelerating electron beam potentials up to 10 kilovolts. Inconsistent data resulting from these tests indicated the need for better electron beam stability and for the reduction of uncertainty in accelerating potentials.

Operating the equipment at low excitation potentials revealed a significant drift in the electron beams current density. The following alterations were made to the original high voltage power supply to reduce this effect.

The filament voltage control was replaced with a precision 10-turn potentiometer.

Thermal couplings were inserted between transistor pairs in the differential amplifier to minimize temperature differences between pairs.

A heat sink was installed in the operational amplifier.

In order to monitor the 10 kilovolts or less acceleration potential precisely, a digital voltmeter was installed on

the electron microprobe (Figure 1). The circuitry (Figure 2) was designed so that the floating 100-megohm input to the meter would be a direct function of, and proportional to, the output voltage of the high voltage power supply. In addition, the unused segments of the rear connectors on the digital voltmeter were wired into a HIGH-LOW RANGE switch to provide a decimal point control.

Calibration Techniques

The amount of uncertainty in the accelerating potential was minimized by calibrating the high voltage power supply and digital voltmeter simultaneously. This was accomplished by connecting a electrostatic voltmeter directly to the output terminal of the high voltage power supply. The electrostatic voltmeter had been calibrated to an accuracy of 1 percent.

The electron microprobe calibration procedure consisted of adjusting the high voltage power supply to a designated potential on the standardized electrostatic voltmeter and tuning the digital voltmeter to that potential. The resulting data from 1 to 20 kilovolts are shown in Table 1. When the 1 percent full scale deviation of the standard voltmeter was combined with the measured deviations of the digital voltmeter, it was determined that the uncertainty of the accelerating potential from 1 to 10 kilovolts was less than 200 volts. With this small uncertainty in accelerating potential, Beaman and Isasi² reported that minimal errors in quantitative elemental concentrations of thin films could be expected. Preliminary quantitative EPA of tantalum-nitride films are discussed in the last section.

Measurement of Beam Diameter

The beam diameter is normally determined by sweeping the focused electron beam across a sharply defined sample edge and measuring the distance required for the beam to move off the sample edge. This sweeping is viewed as a profile of the secondary electron image on the master oscilloscope. After first aligning the sample edge in the scanning electron image with the center of the oscilloscope grid, the distance traversed by the beam in the profile mode is measured directly from the grid of the master oscilloscope. For example, at 10,000 times magnification the distance of one centimeter on the oscilloscope denotes a beam diameter of one micrometer.

Prior to the thin film analysis at low kilovolt excitation potential, a 25 micrometer tantalum foil with a well defined edge

Figure 1. Location of Digital Voltmeter on Electron Microprobe

NOTE: METER DID NOT COME WITH EXTERNAL DECIMAL POINT CONTROL.
DECIMAL POINT CIRCUITS WIRED TO TERMINALS C, D, AND E ON REAR

Figure 2. Diagram of Digital Voltmeter Installation

Table 1. Results of Calibrating Acceleration Potential

Low Range			High Range		
Standard Potential (kV)	Digital Voltmeter (kV)	Deviation (Percent)	Standard Potential (kV)	Digital Voltmeter (kV)	Deviation (Percent)
1.0	1.001	0.1	6	5.92	-1.3
1.5	1.513	0.8	7	6.91	-1.3
2.0	2.001	0.05	8	7.90	-1.2
2.5	2.495	-0.2	9	8.91	-1.0
3.0	2.994	-0.2	10	9.92	-0.8
3.5	3.498	-0.057	11	10.90	-0.9
4.0	3.998	-0.05	12	11.94	-0.5
4.5	4.505	0.1	13	12.93	-0.5
5.0	4.994	0.12	14	13.91	-0.6
			15	14.92	-0.5
			16	15.93	-0.4
			17	16.93	-0.4
			18	17.97	-0.2
			19	18.98	-0.1
			20	20.00	0

was used for beam size measurements. The actual values obtained with the beam current held constant at 15 nanoamperes are shown in Table 2.

Table 2. Beam Size Calibration

Accelerating Potential, (Kilovolts)	SEM Magnification	Grid Distance (Millimeters)	Beam Size (Micrometers)
2.0	2000X	5.0	10
3.0	2000X	4.0	8
3.5	2000X	3.5	7
4.0	2000X	3.0	6

It should be noted that these beam diameters are considerably larger than the normal 0.2-micrometer beam size of the electron microprobe when it is operated at 20 kilovolts and 5 nanoamperes sample current. However, the larger incident beam diameter merely affects the diameter and not the depth of the X-ray generating volume (Figure 3).

X-Ray Producing Volume

Samples of tantalum and tantalum-nitride films on glass and aluminum oxide were used to determine the effects of accelerating potential on the X-ray analytical volume.^{3,4} The total counts and peak to background ratios of silicon k-alpha and aluminum k-alpha characteristic X-rays emitted from their respective substrates were measured as a function of the accelerating potential. The average total count for 10-second intervals from six different areas on each sample are recorded in Table 3.

The quantitative data show that an accelerating voltage of less than 4 kilovolts is required to maintain the analytical volume solely within the tantalum and tantalum-nitride films on the glass substrate (Figure 3). Also the data show that the analysis of 500-angstrom tantalum-nitride films on aluminum oxide is not acceptable because of the persistent aluminum k-alpha counts. This indicates that the rougher surface of the alumina substrates prevents the X-ray generating volume from being restricted to the tantalum-nitride film.

Figure 3. X-Ray Producing Volume for Tantalum-Nitride Films

Table 3. Intensity Measurement of Emitted X-Rays From Substrate Materials

Sample Number	Approximate Tantalum Nitride Thickness (Angstroms)	Approximate Nitrogen Composition (Weight Percent)	Average Si K-Alpha Total Count After 10 Seconds for Glass Substrate Materials at Indicated Accelerating Potential						
			20 kV	15 kV	10 kV	8 kV	6 kV	5 kV	4 kV
1	2000	0	2941	1040	124	62			
2	2000	0.95	2645	1008	111	53			
3	2000	2.5	3089	1321	146	59			
4	2000	3.0	2942	1152	128	53			
5	2000	6.0	4174	2018	297	77	34		
6	500*		5354	3613	1363	505	94	37	23
			118**	102	60	54	33	33	23
			Average Al K-Alpha Total Count After 10 Seconds for Alumina Ceramic Substrate Materials at Indicated Accelerating Potential						
			10 kV	5 kV	2.5 kV				
7	500		12756	855	26				
			151**	29	17				
*Test specimen from normal production run									
**Last number in column indicates background intensity									

Tantalum M-Alpha Response

When the acceleration potential is maintained at less than 4 kilovolts, the characteristic X-rays generated in the analytical volume of the 500-angstrom-thick deposit represent the tantalum and tantalum-nitride materials without interference from the glassy substrates. Although this accelerating potential assures that the X-ray generating volume is within the thin film deposit, it is also important to establish what count rates and peak-to-background ratios are required to provide quantitative electron microprobe analysis.

According to Birks³ the excitation energy for tantalum M-Alpha is 2.7 keV. Therefore, the response of tantalum X-ray was measured between 2 and 3 kilovolts from a 99.99 + percent pure tantalum foil (25 micrometers thick). The resulting data showing the total counts for 10 second intervals and peak-to-background ratios (L+B/B) are illustrated in Figures 4 and 5 for the focused and defocused beam respectively. Since the defocused beam effectively irradiates a larger area of the thin film's surface, the lateral dimension of X-ray generating volume

Figure 4. Tantalum M-Alpha Response to Accelerating Potentials Between 2 and 3 Kilovolts for a Focused Beam

is increased. Figure 4, which corresponds to the focused beam, shows a leveling in peak-to-background ratio between 2.3 to 2.8 kilovolts, whereas the defocused beam (Figure 5) shows a plateau from 2.4 to 2.6 kilovolts in the peak-to-background ratio curve. However, most of the response below the 2.7 kilovolt threshold is primarily instrument noise, with a linear counting rate occurring above 2.7 kilovolts (Figures 4 and 5). Linearity in the peak to background ratios was initiated for the focused and defocused beam at 2.9 and 2.8 kilovolts, respectively. Consequently, 2.85 kilovolts was selected as the minimum accelerating potential to assure consistent data.

Computer Reduction of Data

The measured tantalum M-alpha intensities at 2.85 kilovolts were reduced to provide quantitative elemental analyses of the tantalum-nitride films. Input to the program included the microprobe take-off angle (52.5 degrees [0.916 radians]), the accelerating potential, the tantalum M-alpha characteristic line, and the count rates and intervals for the standard, the samples, and

Figure 5. Tantalum M-Alpha Response to Accelerating Potentials Between 2 and 3 Kilovolts for a Defocused Beam

the background levels. Computer calculated elemental tantalum and nitrogen (by difference) contents are listed in Table 4. The nitrogen contents for the 2000-angstrom films agree reasonably well with their respective amounts in the argon-nitrogen gaseous mixtures used in the reactive sputtering process. It is believed that the major discrepancy between the EPA and bottle nitrogen contents can be attributed to the actual flow patterns of tantalum and argon-nitrogen mixtures to the substrates during the reactive sputtering. In addition, the amount of experimental error of the EPA analysis must also be determined with prepared tantalum-nitride standards. As reported by Colby,¹ these experimental errors were 2 to 4 percent relative to the amount present.

A typical 500-angstrom tantalum-nitride film test specimen on a glass substrate (Sample 6) was chosen from a normal production run and analyzed under similar conditions. The computer calculated results showed that even a 500-angstrom deposit can be analyzed quantitatively. However, the elemental contents of the 500-angstrom tantalum-nitride films on alumina ceramic substrates cannot be determined under the above conditions because of the interference from the aluminum K-alpha X-rays.

Table 4. Computer Reduction of Data

Sample Number	Tantalum Thickness (Angstroms)	Nitrogen Content of Input Gas Mixture (Weight Percent) N ₂	Computer Calculated EPA Results (Weight Percent)	
			Ta	N ₂
1	2000	0	100.00	0
2	2000	0.95	99.27	0.73
3	2000	2.50	96.95	3.05
4	2000	3.00	96.44	3.56
5	2000	6.00	93.14	6.86
6	500		97.37	2.63

ACCOMPLISHMENTS

A method was developed for using the electron microprobe for elemental analyses of tantalum-nitride films. Quantitative tantalum and nitrogen contents were obtained for 500- and

2000-angstrom films deposited on glass substrates. The developed method provides a means to monitor the reactive sputtering process used in the production of hybrid microcircuits. In addition, the overall performance of the microprobe was improved by modification and calibration of the high voltage power supply and digital voltmeter.

FUTURE WORK

Future work will include refinement of the quantitative elemental analysis of tantalum-nitride films on glass and various aluminum oxide substrates. This will include the development of standards of tantalum-nitride material in order to determine the relative error of the EPA. In addition, further modification of the electron microprobe will be pursued to allow an on-site computer for reduction of data and instrumental operation control.

REFERENCES

¹J. W. Colby, *Advances in X-Ray Analysis*, Volume 11, New York: Plenum Press, 1968, p 287.

²D. R. Beaman and J. A. Isasi, "Electron Beam Microanalysis--Part II," *Materials Research and Standards*, December, 1971, p 16.

³L. S. Birks, *Electron Probe Microanalysis*, 2nd edition. New York: Wiley Interscience, 1971.

⁴C. A. Anderson, "Electron Probe Microanalysis of Thin Layers and Small Particles With Emphasis on Light Element Determinations," *Electron Microprobe*, New York: Wiley Interscience, 1966.

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MECHANICAL: Thin Film Analysis

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