Using SPV for Wet Deck Management?
Beware of Unseen Contamination

By Dr. Hugh Gotts

Introduction
Surface Photovoltaic Spectroscopy, or SPV, measurements are widely used to determine the minority carrier diffusion length of semiconductors. The transport of minority carriers determines the behavior of the p-n junctions that are ubiquitous in semiconductor devices. SPV measurements are very useful for iron and sodium content which are directly related to device performance. However, recent studies by Balazs have revealed that other metallic contaminants not detected by SPV are equally detrimental. This article summarizes the Balazs case study experiment and results using various measurement techniques to capture additional metallic contamination data, and key elements to controlling metallic contamination in your process.

As device geometries continue to shrink, the risk of device malfunction due to microcontamination throughout the process also increases. One of our objectives at Balazs is to lead the industry in identifying contamination sources and developing techniques to analyze microcontamination issues. Continuous discovery of wafer defects due to metallic contamination prompted the initiation of this study to define how various metallic contamination in chemical baths impacted the wafer. Since bath processing can account for up to 25% of total process steps, it is a logical place to optimize contamination control.

The basic design of the experiment involved intentionally contaminated bath solutions. Wafers were exposed to the baths and analyzed using different techniques to assess the impact on the wafer and compare analytical methods.

Chemical Baths
As shown in Table 1, the baths tested in the study were SC1 or APM (particle removal), SC2 or HPM (metallic removal), HF (surface oxide etch) and SPM or Piranha (organic removal, clean-up prior to tube processes). New process bath containers were pre-cleaned, the cleanliness assessed, and then filled with various solutions.

	SC2	SC2	SC1	HF	SPM
Chem A (Liter)	0.5L HCl	0.5L HCl	0.5L NH4OH	5.0Gal 10:1 HF	5.7L H2SO4
Chem B (Liter)	0.5L H2O2	0.5L H2O2	0.5L H2O2	2.0L pump HF	0.3L H2O2
Water (Liter)	5.0L H2O	5.0L H2O	5.0L H2O	0.0L H2O	0.0L H2O
Ratio	1:1:10	1:1:10	1:1:10	1:10	19:1:0
Volume (Liter)	6.0	6.0	6.0	20.9	6.0

Table 1: Bath compositions

Intentional Contamination
Known concentrations of 8 different metals were added to each bath. The metals used were; aluminum (Al), calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni) and sodium (Na). Table 2 shows the makeup of each bath after addition of the contaminants.

	SC2	SC2	SC1	HF	SPM
Chem A (Liter)	0.5L HCl	0.5L HCl	0.5L NH4OH	5.0Gal 10:1 HF	5.7L H2SO4
Chem B (Liter)	0.5L H2O2	0.5L H2O2	0.5L H2O2	2.0L pump HF	0.3L H2O2
Water (Liter)	5.0L H2O	5.0L H2O	5.0L H2O	0.0L H2O	0.0L H2O
Ratio	1:1:10	1:1:10	1:1:10	1:10	19:1:0
Volume (Liter)	6.0	6.0	6.0	20.9	6.0
60 ppm Spike A (mL)	2.5	10	1	3.5	1
60 ppm Spike B (mL)	2.5	10	1	3.5	1
Contaminants (ppb)	25	100	10	10	10

Table 2: Bath compositions plus metallic contamination

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Analytical Techniques
As discussed, SPV measurements are widely used but fail to adequately detect metallic contaminants other than iron and sodium. In addition to SPV, this study employed the use of Total Reflection X-Ray Fluorescence (TXRF) and Vapor Phase Decomposition ICP-MS (VPD ICP-MS).

SPV
Wafer surface photovoltage measures the change in the potential due to illumination. Data can be related to metallic contamination. The process requires an oven or RTP activation step.

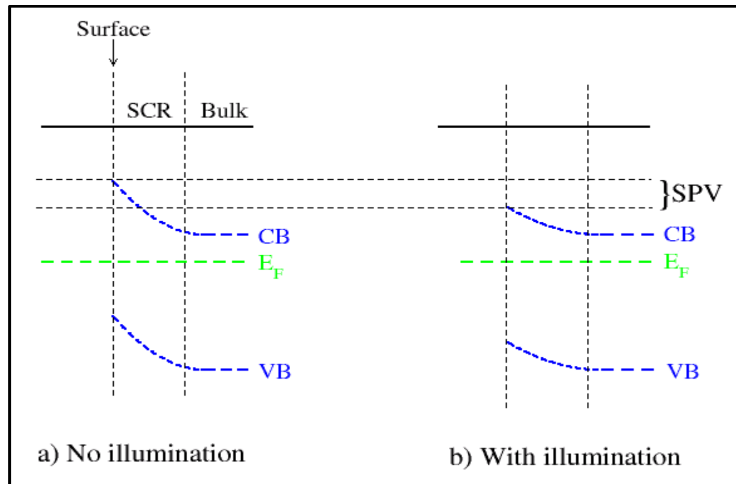

Figure 1: SPV measures the change in potential due to illumination. (Schroder, Dieter K. (2006). Semiconductor Material and Device Characterization. Wiley-IEEE Press and Wikipedia)

VPD ICP-MS
Essentially, VPD is the process of exposing a wafer surface to etching for a specified period, causing dissolution of the surface. From there, collection and analysis of the sample vary. For this study, VPD was used prior to ICP-MS analysis and TXRF analysis. In preparation for ICP-MS analysis a scanning droplet is used to collect the dissolution residue to generate the sample. The sample is then analyzed via ICP-MS for trace metals. (Figure 2)

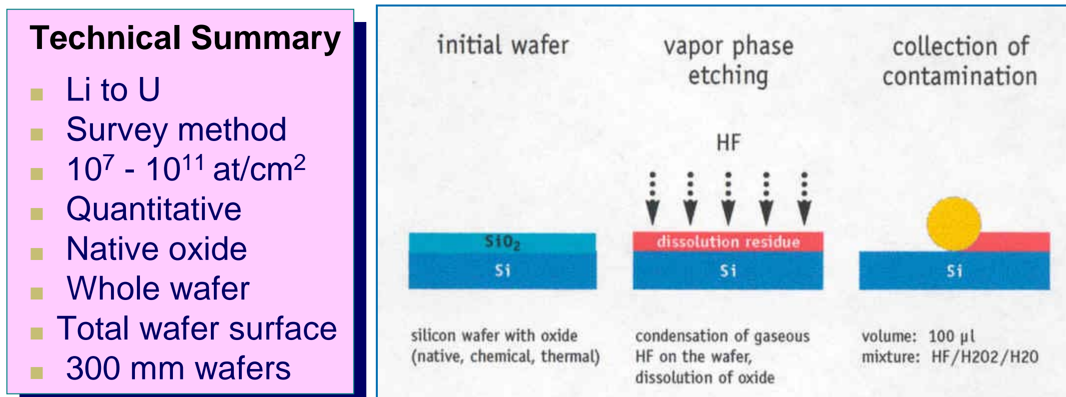

Figure 2: VPD-ICP-MS key facts (left) and VPD preparation for ICP-MS analysis (right)

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TXRF

Emission of characteristic x-rays from a surface is the core principle in XRF analysis (Figure 3). The technique generates spectra (Figure 4) that provide qualitative and quantitative results. Figure 5 illustrates the detection limits of chromium and molybdenum sealed tubes.

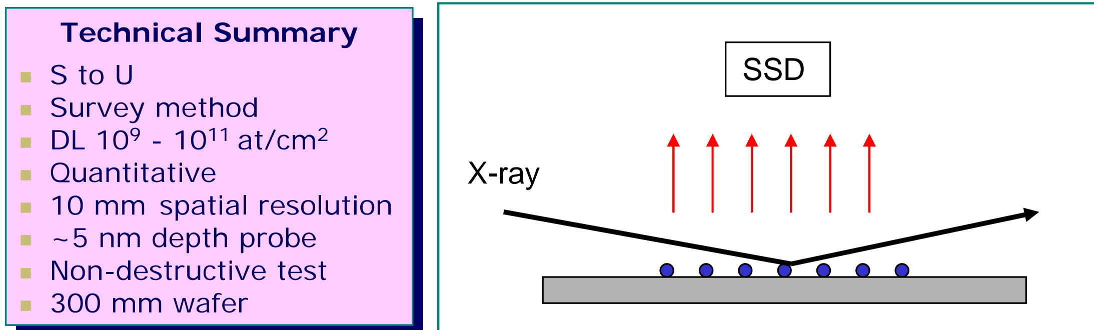

Figure 3: TXRF key facts (left) and basic functionality (right). The critical angle is inversely proportional to the X-ray energy and proportional to the square root of the electron density of the matrix

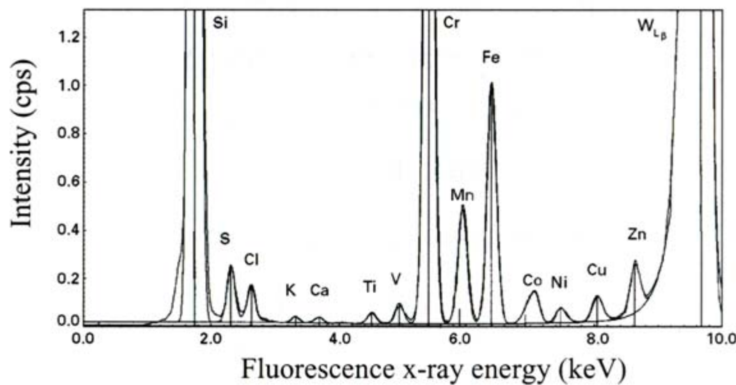

Figure 4: Example of a TXRF spectrum

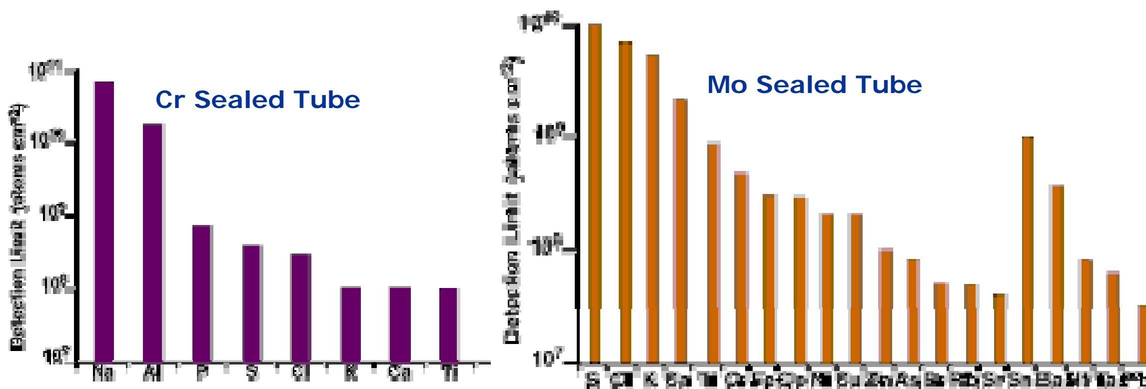

Figure 5: Detection limits of different X-ray sources

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Exposure and Results

150mm FZ wafers (required for SPV measurements) and CZ wafers were dipped in the baths, rinsed, dried and analyzed. The results, shown in Table 3 and 4, illustrate the impact of these metallic substances on the wafer.

$e^{10}*cm^{-2}$	25 ppb SC2					100 ppb SC2				
	CZ	FZ	FZ	CZ	FZ	CZ	FZ	FZ	CZ	FZ
	TXFR	TXRF	SPV	VPD	VPD	TXFR	TXRF	SPV	VPD	VPD
Na	*	77.0	0.75	4.30	1.97	*	76.0	0.71	2.40	6.36
Al	85	142	-	8	30	93	141	-	7	70
Ca	5.58	2.49	-	9.97	7.86	4.98	*	-	3.31	13.6
Cr	*	*	-	*	0.15	0.57	*	-	0.21	0.42
Fe	0.50	1.12	13.6	0.51	3.77	1.08	1.19	65.1	1.91	7.58
Co	*	*	-	0.03	0.16	*	*	-	0.25	0.25
Ni	0.63	0.45	-	0.20	0.45	0.58	0.45	-	0.32	0.51
Cu	*	*	-	0.20	0.39	0.57	*	-	0.40	0.64

Table 3: SC2 bath results at 25ppb and 100ppb contamination levels

$e^{10}*cm^{-2}$	10 ppb SC1					10 ppb HF					10 ppb SPM				
	CZ	FZ	FZ	CZ	FZ	CZ	FZ	FZ	CZ	FZ	CZ	FZ	FZ	CZ	FZ
	TXFR	TXRF	SPV	VPD	VPD	TXFR	TXRF	SPV	VPD	VPD	TXFR	TXRF	SPV	VPD	VPD
Na	*	83.2	0.28	2.97	4.52	*	81.1	0.26	*	1.69	584	79.1	26.7	218	23.6
Al	2590	1300	-	2150	889	63	544	-	0.13	384	1080	139	-	15	25
Ca	6.53	4.12	-	8.05	12.0	3.86	*	-	*	1.43	4.31	*	-	36.7	15.2
Cr	0.43	*	-	0.15	0.19	0.37	*	-	*	0.13	*	*	-	-	0.13
Fe	230	140	23.5	562	377	0.51	29.0	55.9	*	92.8	0.30	0.77	5.64	0.66	7.11
Co	*	*	-	8.39	1.95	*	*	-	*	0.37	*	*	-	0.19	0.14
Ni	1.38	0.25	-	2.32	1.47	0.74	0.40	-	*	0.84	0.63	0.53	-	0.58	1.45
Cu	0.63	*	-	3.04	0.53	*	*	-	0.62	1.59	*	*	-	0.68	0.32

Table 4: SC1, HF and SPM bath results at 10ppbcontamination levels

Conclusions

In conclusion, the data showed that VPD ICP-MS and TXRF provide beneficial data regarding metallic contamination in process baths.

- VPD and TXRF can both provide rapid data (~4 hours).
- VPD provides excellent sensitivity with limited spatial resolution.
- TXRF provides good spatial resolution with lower sensitivity.
- SPD is still useful for Na and Fe analysis

Establish a Baseline

In light of this experiment process yields be improved by correlating bath contaminant levels with wafer surface metal levels. Depending on the process, acceptable levels of various metals will differ. Establishing a baseline of metallic concentrations in baths will aid optimizing bath life, ensure compatibility of bath components, establish a protocol to define acceptable levels of metallic components that impact product performance.

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