Accuracy in Trace Analysis

These data allowed the identification of products arising from ring oxidation, ring attack, side chain oxidation, and photo-Fries reactions.

References

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Analytical Chemistry and Material Purity in the Semiconductor Industry

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Analytical chemistry has evolved from a "hodge-podge" of empirical ideas into a highly visible, diverse and ubiquitous science. Perhaps the two most important industries that place significant demands on analytical chemistry are the biomedical and semiconductor fields. One can envisage a symbiotic relationship between analytical chemistry and the semiconductor industry. While improved analytical methods and instrumentation are constantly needed to support technological progress, it is technology development that provides the impetus and tools for enhanced instruments and thereby, analytical methodology.

The electronic revolution has resulted in significant miniaturization of devices on integrated circuits with complex multi-level structures. A typical VLSI circuit may contain up to a million devices! Obviously, this degree of complexity raises concern of yield, quality, and reliability. Materials play a critical role in these issues with the type and purity of the material directly influencing the profitability and very survival of semiconductor industries. For example, capacitance-voltage shifts caused by mobile ion impurities and ionization effects resulting from alpha-particles destroy the integrity of the devices. Table 1 shows the diversity of materials and their applications.

Table 1. Materials and their applications Thermal print heads Optical disks Te CaF₂ Ta₂O₅ Au SiC Bi AL SiO₂ Cr Al TaN Rh And alloys of above Thin film heads Hard disks----Winchester type Ni-Fe Al_2O_3 SiO₂ Ni-Fe Fe-Si-Al Au Co-Ni Cr Ni-V SiO_2 Co-Cr Al C Co-Ni-Cr Integrated circuits Optical magnetic disks Al(Al-Si, Al-Cu, Gd-Co Al-Si-Cu) Tb-Fe Si Mo & MoSi-AF W-Ti Ta & TaSi₂ SiO₂ W & WSi₂ SiO₂ Th-Co-Fe Au Ti & TiSi₂ Pt Doped Si And other alloys Liquid crystal displays Thin film hybrids ITO SiO₂ Cr Au ATO Ni-V TaN Al_2O_3 Doped ZnS w-Ti Al Та In-Sn Metal Resistors Image sensors Hybrids Monolithic Ni-Cr Al-Ta ITO CrCr-Si In-Sn Al Cr/Cr_2O_3 SiO_2 Ni-Cr-Si Cr-SiO₂ Ni-Cr-Al

The enormous significance of material purity, however, is unfortunately clouded with the current practice of defining purity. At best, the purity phenomenon exists in a very arbitrary manner with its use subject to a myriad of interpretations. Purity of material in the semiconductor industry generally refers to the extent of the absence of impurities in the material. This then introduces the concept of total purity.

Accuracy in Trace Analysis

The ambiguity in purity data stems from the arbitrary and injudicious use of nine's without reference to acceptable and defined specifications. This method yields total purity by simply cumulative total impurity level from 100% to give the data in nine's. This is shown in table 2. It all seems too easy and simple! What does it mean? Was a six nine's (99.9999) pure material exhaustively analyzed and found only to contain 1 ppm total impurity out of all possible contaminants?

Table 2. Classification of purity by use of nine's

Three nine's	 3N	 99.9%	 1000 ppm	impurities
Four nine's	 4N	 99.99%	 100 ppm	impurities
Five nine's	 5N	 99.999%	 10 ppm	impurities
Six nine's	 6N	 99.9999%	 l ppm	impurities

The system of defining, describing, and interpretating purity data needs to be modified. Such changes should be brought about by joint efforts of National Organizations, such as, NBS and ASTM in conjunction with material suppliers and users. Material purity, however, cannot be considered as an isolated issue. It is intricately linked to all the processes and techniques utilized to generate and guarantee the purity data. Table 3 lists some of the areas that are related to the whole concept of purity.

Table 3. Considerations in the purity debate

Semantics	_	Meaning Comprehension/interpretation
 Specifications 	—	Reference to purity Needs and material application
Measurement process	—	Techniques Related functions
 Data reduction 		"Numbers" game
Data communication	_	Analytical terminology Certification of purity actual vs typical Correlation of purity data
Reliability	—	Laboratory QC SPC Process stability and purity

Specifications that define purity are generally built with the manufacturing capability in conjunction with the material application. These specifications must be realistic and clearly defined with a critical list of parameters for evaluation; for example, a critical elemental list. The use of nine's may then become more practical. Perhaps the most important area in this purity debate is the analytical process. Poor analytical practice and techniques generate useless data that distort the information. The analytical chemist is fortunate to have an impressive repertoire of modern techniques to discharge these responsibilities. Such techniques range from the simple potentiometric ion selective electrodes to the sophisticated glow discharge mass spectrometer. It is interesting to note that the choice of technique can have a direct influence on the purity in terms of the sensitivity and detection limits of the methods.

The interpretation and communication of the analytical data introduce the "numbers game." Data manipulation cannot be done without clearly defined conditions. Significant figures, use of absolute or rounded-off numbers, allowable deviations from the specified limits, etc., influence the final result and therefore, the purity. Confusion also arises from use of analytical parameters that are not in accordance with regulations, if any. For example, detection limits are being used with two and three standard deviations. Certification of the analytical data must indicate the use of actual results as opposed to typical values. The use of actual analysis data is more practical in terms of the risks involved and users of high purity materials must be aware of the significant difference in these numbers in their material and supplier evaluation.

The other critical consideration in the purity debate is the subject of reliability. Basically, this involves the need for comprehensive analytical quality control. Table 4 describes some of these parameters which include both internal laboratory and external control. Constant monitoring of accuracy and precision of procedures and data in conjunction with other aspects of the analytical process should be established as standard operating procedures. The use of reference samples and duplicates in analysis are absolutely critical for reliability which in turn produces real and useful information on material purity. A recent trend in the industry is the growing need for statistical process control (SPC). Obviously, SPC cannot be effectively utilized without accurate and precise data. Control charts are now necessary for certification of material purity! Material purity data is now being integrated with the actual process stability to monitor consistency.

The criticality of material purity, therefore, demands that the concept be clearly defined and specified for effective use and correlation of purity

Accuracy in Trace Analysis

data. This discussion highlights the issues that need to be resolved and focused on the role of the analytical chemistry in the process.

 Table 4. Reliability of the analytical process

Analytical quality control
Sampling
 * Valid methods statistics
 Sample/data management
* Accountability
* Traceability
* Automation—LIMS
* Terminology and interpretation of data
Internal quality control
* Procedures
* Accuracy
* Precision
* Facilities/personnel
• External quality control
* Round Robin Studies
* Accreditation
Statistical process control
Process stability
• Purity vs consistency
• •

Determination of Traces of Uranium and Thorium in Microelectronics Constituent Materials

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1. Introduction

Because of the problem of soft errors due to α -particle emission by uranium and thorium [1], determination of trace amounts of these metals in microelectronics constituent materials has recently gained considerable attention. In the present paper, four different techniques: chemical analysis (CA),

instrumental neutron activation analysis (INAA), glow discharge mass spectrometry (GD/MS), and inductively coupled plasma mass spectrometry (ICP/MS) were studied using high-purity aluminum samples A, B, and C.

2. Experimental

2.1 Chemical Analysis

Samples (1-5 g) were decomposed with nitric and hydrochloric acids, evaporated to dryness, dissolved in nitric acid and subjected to chemical analysis.

2.1.1 Uranium Analysis [2,3] With sodium nitrate and aluminum nitrate added into nitric acid solutions of samples, uranium was extracted twice with a carbon tetrachloride solution of tributyl phosphate (TBP). The organic phase was back-extracted thrice with dilute hydrochloric acid after being washed with a sodium nitrate solution and hydrochloric acid. The aqueous phase was evaporated to dryness. The residue was fused with the addition of a fusing mixture consisting of potassium carbonate, sodium carbonate and sodium fluoride. The fused product was set in a fluorophotometer to determine the uranium by measuring the fluorescence intensity at 556 nm.

2.1.2 Thorium Analysis [4,5] Aluminum nitrate and EDTA were added to nitric acid solutions of samples and the resulting solutions were extracted twice with mesityl oxide. The organic phase was back-extracted thrice with water. The aqueous phase, with acids added, was decomposed by heating. The residue was dissolved in hydrochloric acid and with Arsenazo III added to this solution, thorium was determined by measuring the absorbance at 660 nm.

2.2 INAA

About 5 g of each sample was irradiated for 24 h at a thermal neutron flux of 5.5×10^{11} neutrons cm⁻² s⁻¹. After cooling, the irradiated sample was counted for 10,000 s using a Ge (Li) detector. The cooling time was 6 to 8 days for uranium and 15 to 19 days for thorium. Uranium was determined by measuring γ -rays from 228 keV of ²³⁹Np and thorium from 312 keV of ²³³Pa.

2.3 GD/MS

The instrument used was a commercial GD/MS system (VG 9000, VG Isotopes). A pin-shaped