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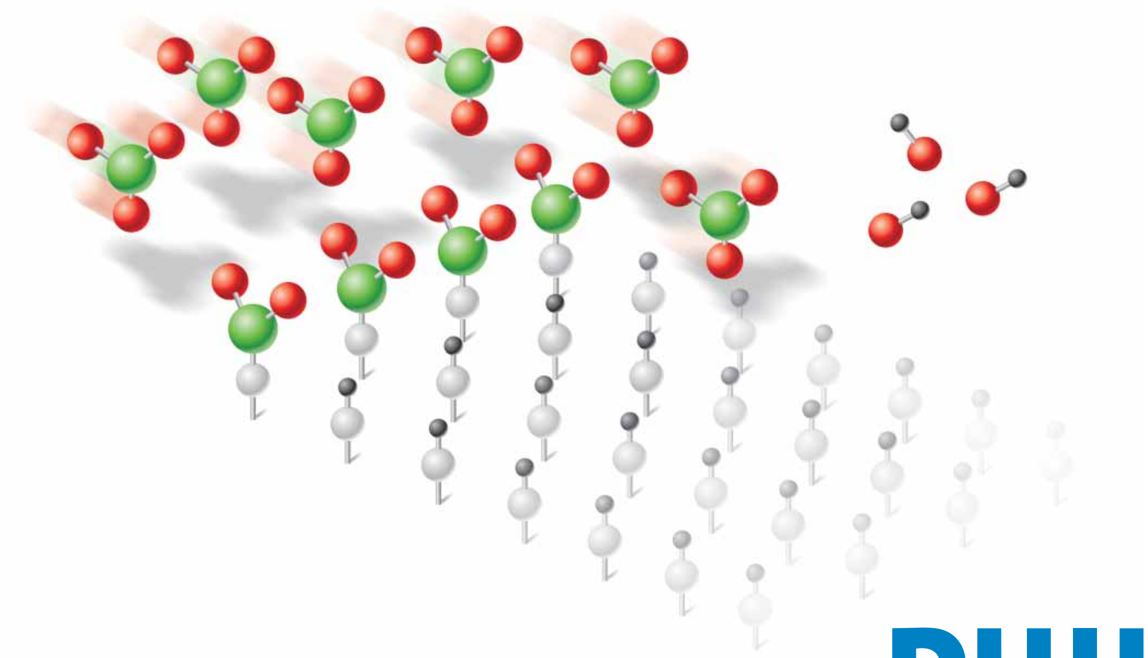
Small variations in the elemental composition of a material can have a major effect on its characteristics. Deviations from normal values are often the source of problems in a production environment. Therefore, quantitative elemental analysis is essential for both problem solving and quality control. For quantitative analysis the bulk of a sample has to be analyzed. Wet-chemical procedures that dissolve the material in strong acids (HCl, HNO_3, $HClO_4$) have to be used. To analyze such solutions, often with high salt concentrations, a very robust analytical technique like ICP-AES is required.

ICP-AES: quantitative analyses,

from sub-atomic layer to bulk composition



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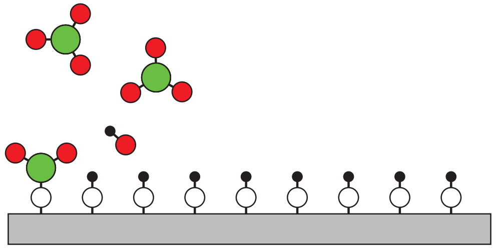


Fig. 1: Precursor molecules react with the surface of the substrate: $AlCl_3$ (g) + Si-O-H (s) ➞ Si-O-$AlCl_2$ (s) + HCl (g).

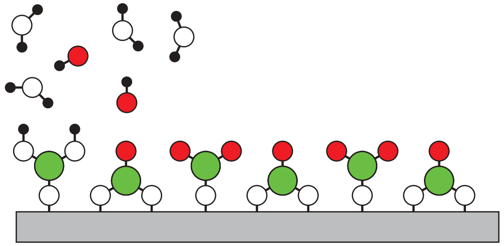


Fig. 2: Water vapor is used to remove the chloride atoms from the surface: $2H_2O$ (g) + Si-O-$AlCl_2$ (s) ➞ Si-O-$Al(OH)_2$ (s) + 2 HCl (g).

Introduction

Analysis by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is usually performed by preparing a sample solution that is transformed into an aerosol by means of a nebulizer. The small droplets in the aerosol are transported through a spray chamber to a high temperature Argon plasma. The plasma effectively atomises and excites the material in the sample to a temperature of 7000 K. This results in free atoms in a higher energy level, which lose that extra energy by emitting light. The element-specific radiation is highly characteristic and can be measured with an optical spectrometer. Because the radiation is very narrow-banded and many emission lines exist for each element, interferences can be easily avoided. Numerous examples of ICP-AES analyses exist, of which two analytical questions will be highlighted in this application note: characterization of atomic layer deposition of Al/Zr on a silicon wafer and the determination of the bulk composition of a phosphor used in displays.

Quantitative analyses of sub-atomic metal oxide layers

Principle

The electrical behaviour of a CMOS (complementary metal-oxide-semiconductor) device is strongly influenced by the silicon oxide layer between the gate and the substrate. In order to successfully replace the SiO_2 dielectric layer with an alternative material, a long list of physical and electrical demands will have to be met. To avoid high leakage currents and still achieve the required capacitance, a material with a higher dielectric constant (high-K) has to be used. Research on alternative gate dielectrics focuses on these aspects, with limited oxide thickness as a prerequisite.

Atomic layer chemical vapour deposition (ALCVD) is a chemical technique, where film deposition occurs through a well defined sequence of surface reactions that are separated from each other by purge steps with an inert gas. Each reaction step is self-limiting since all active adsorption sites become fully occupied. Sequential delivery of the reactants offers a route for precise control of film thickness, stoichiometry and phase formation.

The principle of ALCVD is illustrated in figures 1 and 2, where the chemical reactant $AlCl_3$ (precursor) reacts with a Si-substrate, which has a surface termination of atomic bonds (-O-H). This technique is used to deposit high-K metal oxide films like Al_2O_3, ZrO_2, Ta_2O_3 and HfO_2 (or combinations of these), which have potential to replace the SiO_2 dielectric gate layer.

Fig. 3: Injection of the acid mixture to dissolve the Al/Zr layer.

Analysis

Using ICP-AES analyses, absolute amounts of the deposited elements can be determined with high accuracy. This makes it possible to fine-tune the ALCVD process from nucleation to final layer thickness.

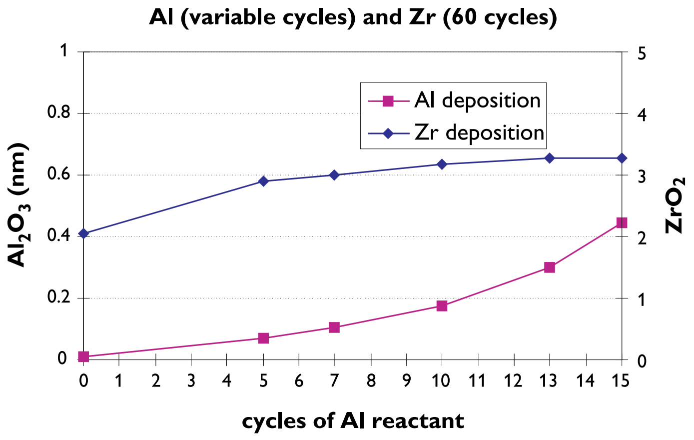
In this particular example a two-layer stack of Al_2O_3 and ZrO_2 was examined. The sub-nanometer oxide layers have to be dissolved before analysis. For this purpose a strong acid mixture (HCl, HF and $HClO_4$) is used. The Si-wafer sample (10 cm^2) is put upside-down (the Al_2O_3/ZrO_2 oxide layer facing downwards) in a platinum vessel, containing a small volume of acid (fig. 3). After 10 minutes at room temperature, the Si-wafer is rinsed with water and discarded.
Subsequently the sample solution is evaporated to dryness under IR-lamps (fig. 4). The residue (soluble perchlorate salt) is dissolved in a small amount of diluted HNO_3. In this solution Al and Zr can be measured quantitatively using ICP-AES. Relative standard deviations of the Al/Zr amount are 1-3%.

These ICP-AES results are transformed to layer thickness for the different compounds in figure 5. From these results the growth behaviour of Al_2O_3 and ZrO_2 can be deduced.

Growth inhibition has been observed for the Al_2O_3 layer. This growth inhibition is attributed to the lack of functional OH adsorption sites on hydrogen-passivated surfaces. The growth of ZrO_2 on top of the resulting Al_2O_3 layer appears to be related to the thickness of this underlying layer. A growth inhibition of ZrO_2 on thin Al_2O_3 layers results.

ICP-AES is a sensitive enough technique to determine only a few % of a monolayer Al_2O_3 or ZrO_2 on a Si-wafer surface. As a result, nucleation and initial film growth can be followed with high precision.

Fig. 5: Initial growth of the Al_2O_3 and ZrO_2 layer on HF-dipped Si.



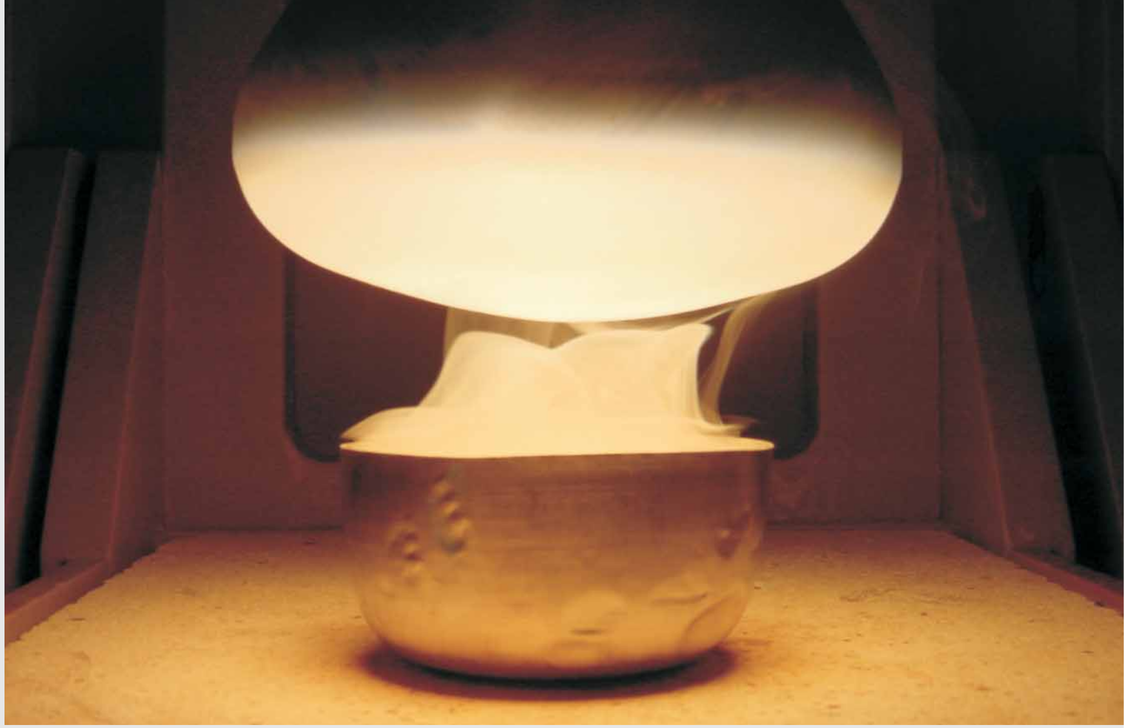


Fig. 4: Evaporation to dryness under an IR lamp.

Elemental bulk composition of phosphors

Phosphors are widely used in CRT displays and flat panel displays. They essentially consist of purified inorganic materials, doped with small quantities of suitable additives, called dopants or activators. These activators are present at concentration levels varying from a few parts per million up to a few percent of the host lattice. The elemental composition of the phosphor determines the colour of the emitted light. This has led to the development of different families of phosphors specifically made for particular applications.

ICP-AES offers the opportunity to exactly determine the elemental concentration of any phosphor, both in terms of main components as well as dopants. Again, a suitable sample solution of the material under investigation has to be prepared. Some phosphors can be readily dissolved in acids. Others can only be decomposed after mixing with another solid (a so-called flux) at a high temperature prior to dissolution in acid.

An example of the latter category is CaS:Eu phosphors. To allow for ICP-AES analysis, these phosphors are molten in a platinum crucible with a sodium carbonate/borate flux (see photo on frontpage).
In this environment sulphur is completely converted to sulphate. The resulting melt can be dissolved in hydrochloric acid and subsequently diluted with water. For quantitative analysis standard solutions are prepared with commercially available certified standard solutions using the same matrix as the sample solutions.

Sample	Ca	Sr	S	Eu	O	Sum
XX 52	50.8	0.56	41.2	0.18	7.9	100.6
XX 53	44.5	0.42	35.8	0.27	19.7	100.7
XY 19	52.3	2.26	43.1	0.41	1.62	99.7
XY 04	51.9	1.79	43.1	1.01	0.96	98.8
XZ 78	53.4	1.29	43.5	0.20	1.18	99.6
XZ 77	30.8	30.5	36.6	0.18	2.17	100.2
XZ 76	17.6	43.6	30.2	0.15	8.6	100.2
XZ 09	6.9	52.2	24.5	0.11	15.8	99.5
XY 03	0.1	62.9	22.5	0.10	14.9	100.4
YZ 83	---	57.6	20.6	0.10	21.9	100.2

Table 1: Composition of a series of typical phosphors in weight %.

Table 1 shows the composition of a series of typical phosphors in weight %. In addition, the oxygen content has been determined with an alternative technique. The sum of the different elements equals 100 ± 1 weight %. This shows the quantitative nature of ICP-AES for both main and minor components.

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