

State-of-the-art in analytical characterization of high purity solid samples by different spectroscopic methods

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Abstract. Facilities and some results of several spectroscopic methods which have potential applications in the field of analysis of solid high purity substances and which have been elaborated in Russia, will be discussed in this paper. Laser nondispersive atomic fluorescence method with glow discharge cathode sputtering atomiser, may be used for trace element determination as well as a tool for the investigation of technological processes, viz. deposition of thin films. Investigations on reduction of a background level in the new hollow cathode ion source for mass-spectrometry have been carried out. Laser mass spectrometry with tandem laser mass reflectron is successfully designed and applied for gaseous impurities determination in high pure silicon with limit of detection of 10^{-3} – 10^{-5} ppm wt. Several results of the layer-by-layer and bulk trace analysis of solids by high resolution mass spectrometry with radio frequency powered glow discharge ion source with the limits of detection at 10^{-1} – 10^{-3} ppm wt will be presented here. The traditional arc and spark emission technique still finds considerable use. One of the examples considered in the paper is the analysis of metalfullerenes. To overcome the calibration problem the fluorination process inside the electrode crater using zinc fluoride has been investigated.

Keywords. Solids analysis; spectroscopic methods.

1. Introduction

Direct analysis of solids is of interest for trace elements determination in high purity substances, ceramics and other difficult soluble materials. It has a number of important advantages compared to the analysis of solution samples, such as lower limits of element detection, less risk of losses and contaminations. However, there are some drawbacks in direct solids analysis. More serious of them are related to calibration and sample preparation procedures. Probably that is the reason why an excellent analytical technique is available for the elemental analysis of solution samples, however, solid state analysis has not kept pace. On the other hand, there are a number of spectroscopic methods which have potential for successful application in this field. Several of them, which have been designed or modified fully or partly in Russia will be considered here.

2. Laser atomic fluorescence method

Atomic fluorescence spectrometry (AFS) is less popular than other spectroscopic methods. It may be explained by various reasons. The main reasons being insufficient knowledge of processes taking place in AFS with analyte as well as with lack of a simple and effective equipment.

At the same time AFS has many advantages as compared to other spectroscopic methods: low DLs, large linear dynamic ranges, multielement capabilities, freedom from spectral interferences, the possibility of nondispersive registration system employment and simplicity. It is known that detection limits in AFS are extremely dependent on an excitation source and type of an atomizer. An atomizer for AFS should provide the stable nebulization–atomization efficiency and maximal fluorescence power yield. It is known that the use of a nondispersive optical registration system permits simplifying the design and lowering cost of the device.

The nondispersive laser atomic fluorescence spectrometer (LAFS) with cathode sputtering glow discharge atomiser, designed at the Institute of Microelectronics Technology and High Purity Materials, Chernogolovka, consists of the following units: sputtering chamber with vacuum and gas-filling systems and power supply for glow discharge; fluorescence excitation system, based on tunable dye-laser (wavelength range for full set of dyes, 440–700 nm, spectral width of the emission line, 0.05 nm) pumped by pulsed eximer laser (wavelength, 308 nm, pulse duration, 20 ns, pulse power, up to 8 MWt); pulsed nondispersive registration system of fluorescence signal based on PMT and boxcar-integrator triggered by photodiode sensor; system of emission spectra registration which includes two optical spectrometers based on CCD (spectral range, 200–700 nm with spectral resolution, 0.1 nm); electronics interface for coupling spectrometer with PC; developed software for spectrometer control

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and digital proceeding of the fluorescence and emission spectra. The design of atomizer is shown in figure 1. The case of atomizer serves as anode and the sample, shaped as a tablet (12 mm in diameter and 4 mm thickness) serves as cathode. Due to significant difference between the anode and cathode surfaces only sputtering of the sample-cathode is enabled. The isolator and metal screen serve to prevent sputtering of the sample holder. The atomizer chamber is blackened on the interior to minimize the scattering of laser radiation, the diaphragms and light trap are incorporated as well. Different parameters of this atomizer have been studied (Grazhulene and Khvostikov 1991) in the quasi-continuous and pulse modes. The sputtering, diffusion coefficients and the density of atomic vapour have been determined. The possibility of increasing the depth resolution in depth profiling down to 10 Å has been shown. The pulse operation mode of the atomizer enables the depth resolution in bilayer analysis to be lowered by two orders of magnitude. The use of the non-dispersive optical system of fluorescence registration and optimization of the optical system of fluorescence collection allowed to obtain limit of sodium in molybdenum detection as 24 ng/g.

Another application of such spectrometer is an investigation "in situ" of sputter etching and deposition technique in thin films processes, for instance, superconductors technology. Namely, comparative simultaneous (atomic-emission and LAES) investigation of gas phase has been carried out by sputtering of yttrium, zirconium and yttri-

um-zirconium alloy samples at varying oxygen partial pressures in the range of $0-5 \times 10^{-3}$ bar. The advantages of this combined method for online monitoring of processes, used in microelectronics have been demonstrated. The correlation in behaviour between emission and fluorescence spectra in wavelength range, 590–620 nm, has been established. The model of the analytical emission and fluorescence signal forming mechanism of metals and their oxides in gas phase at sputtering in glow discharge and laser excitation of fluorescence has been proposed. It was established that the intensities of Y lines decrease and Y_2O_3 increase on increasing partial pressure of oxygen in the range from 1×10^{-5} to 2×10^{-3} bar, that can be controlled by oxidation of Y atoms in glow discharge. Following increase in oxygen pressure the intensities of all lines decrease.

3. Mass spectrometry

3.1 Hollow cathode glow discharge mass spectrometry

The hollow cathode mode of the glow discharge (HCGD) is of particular interest because of its unique properties. The successes of HCGD application in optical spectroscopy showed that stable, reproducible GD source is attainable. The results of investigation of HCGD in mass spectrometry (MS) have been not very satisfactory (Bruhn *et al* 1979) due to high rate of the residue evaporation and instability of the analytical signal. An important problem in MS

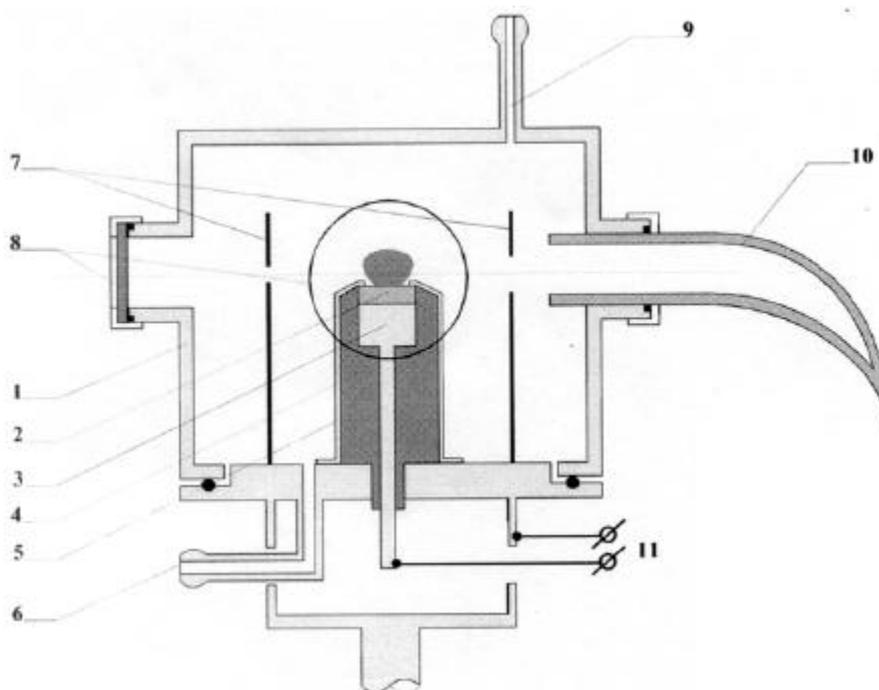


Figure 1. Design of the cathode sputtering atomizer (1. case; 2. sample; 3. sample holder; 4. isolator; 5. screen; 6. argon inlet; 7. diaphragms; 8. quartz windows; 10. light trap).

analysis of solids utilizing HCGD ion source is configuration of the sample and its position inside the HC cavity, extraction of ions and transporting them to the analyser. Investigations on reduction of a background level in the new HCGD ion source for MS designed by Sikharulidze and Lezhnev (2003) allowed us to suggest three ways of background reduction: (i) formation of a plasma “stopper” at the top of hollow cathode; (ii) optimization of glow discharge parameters and (iii) simultaneously with sample sputtering in the discharge chamber of so-called “getter metals” (Ti, Ta, Nb, Zr, W, Ba), which effectively absorb hydrides, gases and hydrocarbons. Combination of all these factors allows to reduce background of a glow discharge source by four–five orders of magnitude. Figure 2 demonstrates the cross-section of HCGD cavity. At definite pressure the plasma penetrates into HC surrounding the sample. In order to prevent the discharge between walls of the discharge box (anode) and cathode, the minimal distance between them should not be $< 1\text{--}1.5$ mm. The orifice (0.5–1 mm) on the opposite side of cathode serves for extraction of ions. Voltage between anode and cathode is 1–2 kV, discharge current, 5–100 mA, discharge voltage, 0.3–1.0 kV.

It was found that the sputtering rate of the sample is by one–two orders of magnitude higher than that for HC walls even at the close values of sputtering coefficients of both materials. Obtained mass-spectra of Cu shows that intensity of Cu line is close to that of Ar and by several orders of magnitude higher than intensity of Al which serves as a cathode material. The ion current of Cu^{63} is 10 nA, i.e. the aperture ratio is sufficiently high. The process of ions extraction and transport from HCGD to the mass-analyser was studied. Ions extraction from discharge area may be explained by the process of ambipolar diffusion. It is established that the electron flow may be significantly enlarged by replacement of a plane diaphragm to the cone one. It leads to an increase of ion current amplitude approximately by five times due to increasing electron current density at the top of cone.

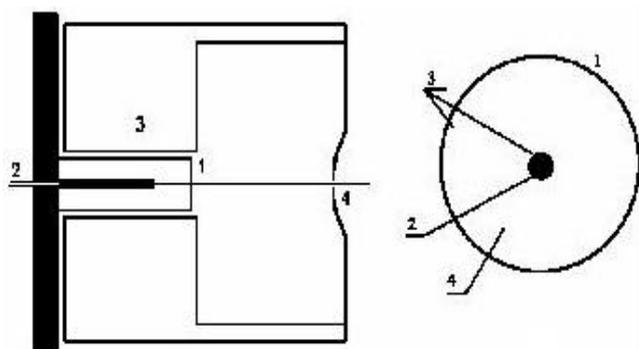


Figure 2. Cross-section of hollow cathode of ion source with a sample (1. hollow cathode; 2. sample; 3. cathode dark space; 4. plasma).

The use of Pierson focusing optics allows additional increasing of resulting aperture ratio of ion source by two orders of magnitude compared to the traditional design.

One of the important problems in MS is analysis of nonconductive materials, viz. ceramics, soil, geological samples, etc. For this purpose, the method of analysed powder compactification using liquid gallium (1–3%) have been elaborated. It was established that ion current of matrix element in this case is lower than that in analysis of conducting materials by about one order of magnitude. However, ion current is stable, which demonstrates the stability of sputtering process. More intensive lines in the mass-spectra of soil belong to Si, Ar, O_2 and H_2O . Contents of Ga does not exceed 1–2% of Si.

3.2 Laser mass spectrometry

The direct laser MS analysis of solids allows to obtain LOD for majority impurities in the range of about 10 ppb. However, determination of very important gaseous impurities (GI) has considerable difficulties connected with surface contaminations and the background adsorption even at the pressure of 10^{-7} torr in the ion source of MS. The technique of GI determination in high purity semiconductors using laser MS with tandem laser mass reflectron (TLMR) has been developed by Bezrukov *et al* (2002, 2004) (figure 3). The technique includes special procedure of surface cleaning by double laser pulse with modulated Q-factor. The method of surface cleaning has been tested using specially prepared samples of silicon covered by silver and reference samples of high pure silicon with known contents of oxygen. It was shown that the laser irradiation effectively deletes primary surface contamination. The removal of six layers provides clearing to the bulk content of oxygen in samples. The registration system provides the separate digital registration of impurity ions and analogue-digital matrix ions registration. Additionally, the special design of the optical system (two reflectors), the electrodynamic valve, which passes only ions of impurities to the second analysing stage permit to reduce LOD of GL in Si, AsS, AsSe, ZnSe and metals up to 1 ppb wt. The linearity of calibration curves has been obtained in the concentration range 0.1–100 ppm wt. The relative standard deviation does not exceed 0.23. Accuracy of measurements has been tested using reference materials.

3.3 Mass spectrometry with radio frequency powered glow discharge ion source

Combination of an RF-powered glow discharge ion source with high resolution mass spectrometers (HR-MS) is the most promising technique for the direct analysis of nonconducting materials without dissolution or dilution of a sample (Marcus 1994; Marcus *et al* 1994). The spread of

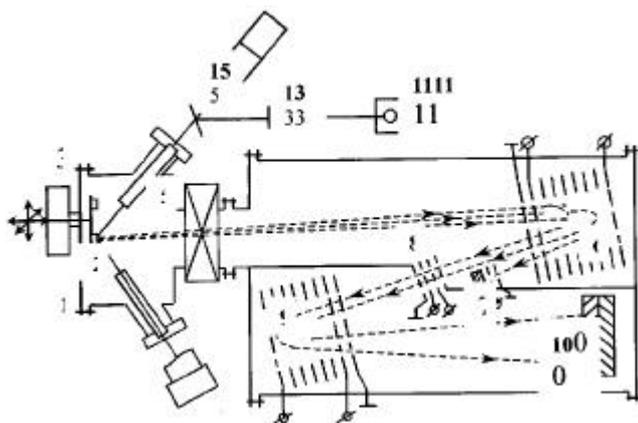


Figure 3. Tandem laser mass reflectron (2. sample; 6,9. reflectors; 7. matrix detector; 8. electrodynamic valve; 10. impurity detector; 15. double laser).

this powerful method is limited by the absence of commercial instruments accessible to analytical chemists.

Magnetically enhanced rf-powered glow discharge ion source (planar magnetron) (RF-GD) has been designed for the double-focusing mass-spectrometer SM-1B (Varian MAT, Germany) with Mattauch-Herzog geometry by Saprykin *et al* (1995a,b). The ion intensities and the energy distribution of the analyte and discharge gas ions have been studied as functions of the discharge gas pressure. The aim of this research was optimization of operating pressure of rf-powered magnetron glow discharge and ion transmission to achieve maximum analyte ion intensities with respect to the intensities of background contaminant ions. It has been shown that maximum analyte ion intensity is observed at argon pressure of ~ 10 Pa. At this pressure, the kinetic energy distribution of analyte ions extracted from an rf-magnetron glow discharge plasma is shifted by ~ 20 eV to higher values compared with the maximum values observed for ion species originating from plasma gas. Thus, an effective energy separation of analyte ions from background contaminant ions can be achieved by adjusting the energy analyser of a double-focusing instrument. Developed RF-GD enabled the layer-by-layer and bulk trace analysis of solids in full range of conductivity: metals, semiconductors: Si, Ge, GaAs, InP etc and non-conductors—with the limits of detection (LODs) at 10^{-5} – $10^{-7}\%$ (for metals and semiconductors) and at 10^{-3} – $10^{-4}\%$ (for glasses and ceramics).

3.4 Arc and spark emission technique

Traditional arc and spark emission technique in some cases still find considerable use. One of the examples is the use of d.c. arc emission for the analysis of quite new substances, viz. fullerenes. These compounds chemically

based on carbon, have very interesting properties due to their specific structure, especially if they consist of metals (as a rule Y and La) interstitial in the crystal lattice. So called metfullerenes have very high boiling temperatures and are difficult to dissolve. Therefore, solids analysis is more preferable in this case. We employed d.c. arc or ICP with electrothermal vapourization for this purpose. As well as in other methods of solids analysis the main problem here is the choice of adequate reference materials (RM). It seemed that RM based on graphite powder should be the matter of choice, however, evaporation curves of La and Y from graphite and fullerene differ. Since La and Y were introduced into the graphite powder as oxides, such difference may be explained by another species of the elements, or fullerene lattice strength. To overcome the calibration problem the fluorination process described in our previous publications for solids analysis (Zolotareva *et al* 1988, 2003) has been investigated. Zinc fluoride (20% mass of powder) was used as fluorination agent. In this case the evaporation curves of La and Y from fullerene and graphite in the presence of ZnF_2 are identical. Therefore, the introduction of zinc fluoride to the solid powders allows determination of Y and La in metfullerene using RM on the base of graphite powder.

4. Conclusions

Nowadays number of spectrometric methods such as inductively coupled plasma have scored a leading position in trace and ultratrace analysis of inorganic substances. Though inductively coupled plasma mass spectrometry (ICP-MS) is widespread, this method is mostly considered as an analytical technique for ultratrace analysis of aqueous solutions. Determination of trace elements in solids at the sub ng/g level concentration by ICP-MS is often limited especially for samples which are very difficult to put into the aqueous solutions such as chemically resistant glasses and ceramics. Another limitation is concerned with purity of chemicals used for sample dissolution and delusion. To determine trace elements in chemically resistant materials, atomic emission, fluorescence, mass spectrometry utilizing hollow cathode glow discharge, laser ion sources are mostly suitable. These methods can provide a direct (without any chemical pretreatment) survey analysis of solids with simultaneous determination of up to 60 impurities at sub $\mu\text{g/g}$ level. To realize the analytical performances of solid state analytical techniques the modifications of traditional technique or development of a new one are necessary.

In this paper, some modifications of such technique providing direct trace analysis of semiconductors, chemically resistant glasses, ceramics and single crystals elaborated and investigated in Russia during the last few years are presented and discussed.

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References

- Bezrukov V V, Kovalev I D, Malyshev K N and Ovchinnikov D K 2002 *Zhurnal Analiticheskoy Khimii* **57** 378
- Bezrukov V V, Kovalev I D, Malyshev K N and Ovchinnikov D K 2004 *Zhurnal Analiticheskoy Khimii* **59** 728
- Bruhn C, Bentz L and Harrison V 1979 *Anal. Chem.* **51** 673
- Grazhulene S S and Khvostikov V A 1991 *Spectrochim. Acta* **B46** 459
- Marcus R K 1994 *JAAS* **9** 1029
- Marcus R K, Harville T R, Mei Y and Shick C R 1994 *J. Anal. Chem.* **A902**
- Saprykin A I, Meichers F G, Becker J S and Dietze H-J 1995a *Fresenius J. Anal. Chem.* **352** 570
- Saprykin A I, Becker J S and Dietze H-J 1995b *JAAS* **10** 897
- Sikharulidze G G and Lezhnev A E 2003 *Zhurnal Analiticheskoy Khimii* **58** 967
- Zolotareva N, Kuziakov N, Khlistova A and Grazhulene S S 1988 *Zhurnal Anal. Khimii* **43** 1199
- Zolotareva N I and Grazhulene S S 2003 *Zhurnal Analiticheskoy Khimii* **58** 504