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UV LED Photo Electron Ionisation for MS and IMS

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Abstract

A new MEMS ionisation source for spectrometry is presented on the basis of photo electron emission in silicon MEMS. Lanthanum hexaboride ceramic sample and thin nanolayer proved their suitability for photo electron emission in the desired photon energy range of 3.1eV to 3.9eV which correspond to industrially available UV LED. This ionisation source alternative to a Photoionisationdetector (PID) is inspected of its gas ionisation behaviour using gases with an ionisation potential over and under an energy of 10,6eV. To enable the ionisation of the gases the emitted electrons were accelerated to a well-defined energy. The results of these investigations are comparable to the UV discharge lamp results. Gases can also be ionised by using accelerated electrons of energy as far as 300eV, which cannot raised by a UV discharge lamp.

Keywords: lanthanum hexaboride, photoemission

1. Introduction

Analytical instruments like mass- (MS), ion mobility spectroscopy (IMS) or photo ionisation detectors (PID) are used for the detection of chemical, biological and nuclear hazardous materials. The fundamental concept of such instruments is based on the ionisation of molecules, various methods e.g. by electric fields and detection of them by ion current measurements. Available methods of ionisation are corona discharge, atmospheric pressure photo ionization (APPI), electro spray ionization (ESI), or the use of radioactive sources such as ⁶³Ni or ²⁴¹Am [1]. Whilst all of them bear specific advantages, new approaches are sought, especially those being capable of energetic addressing distinct ionization levels like two photon ionization as has been recently developed [2].

In this work a miniaturized source is presented which avoids laser equipment and uses photo electron impact ionisation instead. This should not only shrink sizes but bears the same potential of variable, adjustable electron energies and also reduce molecule fragmentation due to high acceleration voltages as normally found in electron impact ionisation sources.

The main task of thin investigation was to find electron emitting materials with low work function even after having been exposed to air and test the ionization arrangement and its limits. The goal of this search should then be to avoid UV discharge sources as the commonly used, short life time 10,6eV Pen Ray lamp and go for UV LED instead. The final step would the result in some miniaturization for admitting functionality up to atmospheric pressure.

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2. Experiments

2.1. LaB_6 electron emissive layers

Materials which are suitable for our photoemission purposes provide enough electrical conductivity, don't oxidise on air nor react with humidity. We chose Borides, like lanthanum hexaboride (LaB_6) or cerboride (CeB_6), which are widely stable compounds against oxidation [3] and are classically predestined for photoemission because of their low work function if conditioned under high vacuum. For thin layers employed in MEMS also their emission properties after oxygen exposure have to be checked and, in general, the layer stability with respect to boron losses, which are known for Silicon and to some extent for quartz substrates.

In order to prevent from unintentional boron losses which reduce the electron emission of the LaB_6 especially from ultra thin, UV transparent films, barrier layers of a thin CoSi_2 were tested proceeding LaB_6 , both deposited by PLD. By means of UPS LaB_6 thin films on sapphire and Silicon with CoSi_2 were compared to the ceramic material under high vacuum, room temperature "as transferred" conditions. The results are depicted in figure 1: Whilst the ceramic disk comes with the lowest work function peak at 2,2eV, followed by 2,7eV for RT processed thin films on Silicon, both of them are weak in terms of quantum efficiency in comparison to thin films deposited at 400 °C with a work function of 3,1eV which is 0,6eV lower than the main ceramic emission peak. Layers deposited on sapphire showed some faint emission only. Whilst the emissivity of the ceramic layer is 6,5 times higher than for hot processed thin films, a significant work function reduction for those films can be gained.

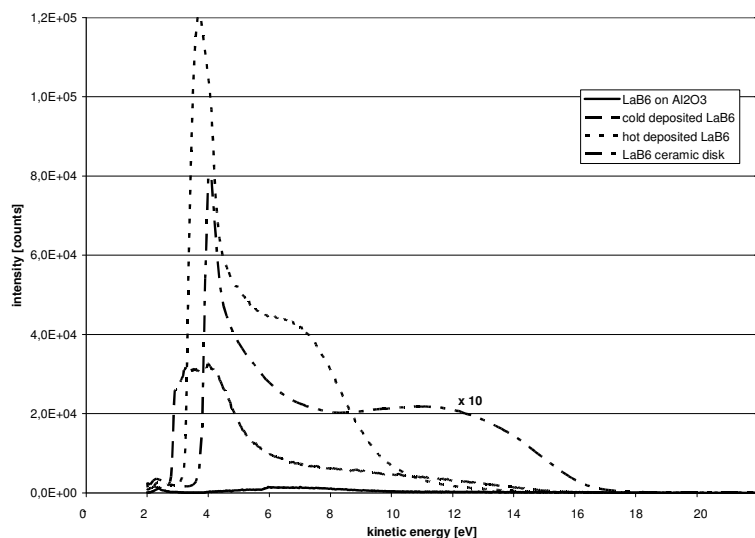


Fig. 1. UPS measurements of LaB_6 on different substrates

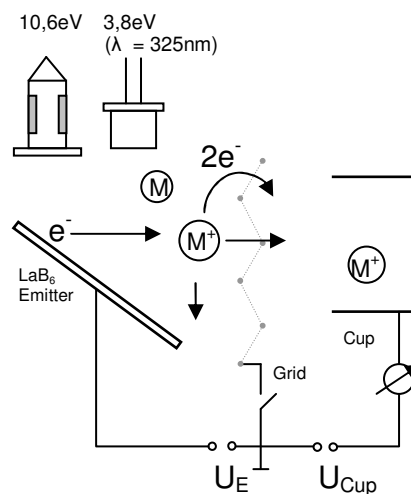


Fig. 2. Block diagram of the measurement setup

2.2. Gas ionization experiments

For ionization testing a setup depicted in figure 2 was brought in a variable pressure test chamber. An UV discharge lamp and a 325 nm UV LED source illuminate the layers for electron emissive, which ionize gas molecules drifting towards a Faraday cup. The gases were directly brought into the evacuated test chamber from liquid substances via a needle valve. The substances used are listed in table 1 together with their ionization energies.

The first test employed the UV discharge lamp running with 10,6eV without any LaB_6 but the collecting Cup connected. Thus, acetone and IPA should be photo ionized whilst the other substances will not be detected. Figure 3 shows the according result given with relative Faraday cup changes in the y-axis. This is changed with voltages applied to LaB_6 : As the difference between $h\nu$ and Φ may be contributing to the kinetic energy of electrons, we

expected some 12eV of ionization potential being available after applying 5V to the system. The according measurement leads toward the middle curve in figure 3, where methanol is starting to be ionized but neither nitrogen nor other air compounds.

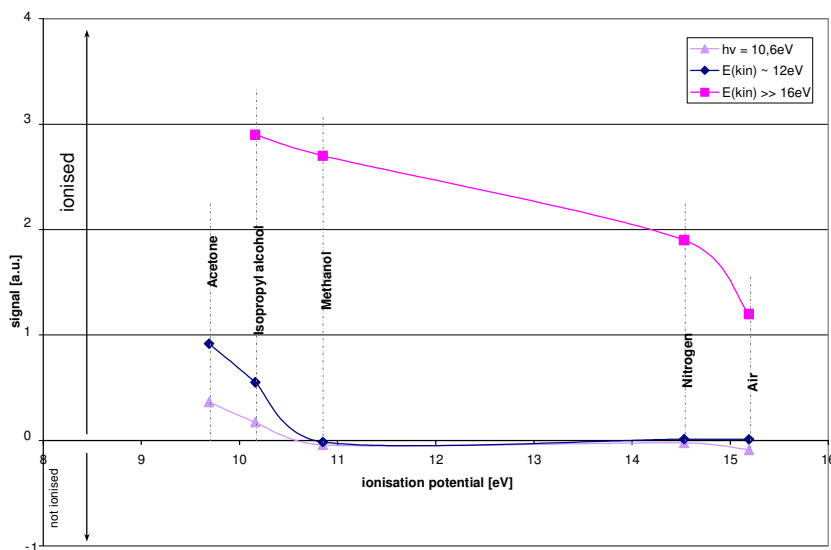


Fig. 3. Dependence on ionisation potential to the difference of current, which was measured at the influx of gases

The next step was to apply strongly higher potentials to the system, in sum 100 Volts, yielding in ionization capabilities exceeding 16eV. Hence nitrogen and other air compounds are detected within the system together with increased sensitivities for the other compounds.

Finally, the 3,8eV LED source has been used for detection of chloroform, which needs ionisation energies of 11,4eV. Whilst the illumination power of the diode was seen far below that of the UV discharge source due illuminating angle restrictions, a clear signal is detected. The original curve of this first test under 50 Volts electrical potential is depicted in figure 4.

Table 1. Used solvents and gases for the ionisation measurements [4]

Substances	Ionization potential [eV]
Air	15,19
Nitrogen	14,53
Chloroform	11,4
Methanol	10,85
Isopropyl alcohol	10,16
Acetone	9,69

3. Discussion

We find LaB6 layers suitable for atmospheric electron emission with necessary illumination energies starting at 3,1eV. This value is slightly lower than earlier findings by May et al [5]. Such values are finally sufficient for LED excitation as shown in the experiment. As the concept of electrical acceleration towards definite energies and thus

“switching on” molecular detection by voltage variation is proven, the question of transferring the concept towards higher pressures is left open. One possible way is to shrink the acceleration path down to the same scale lengths where ionisation occurs, which leads to a miniaturized assembly. Such arrangements are currently evaluated and will be presented at the conference.

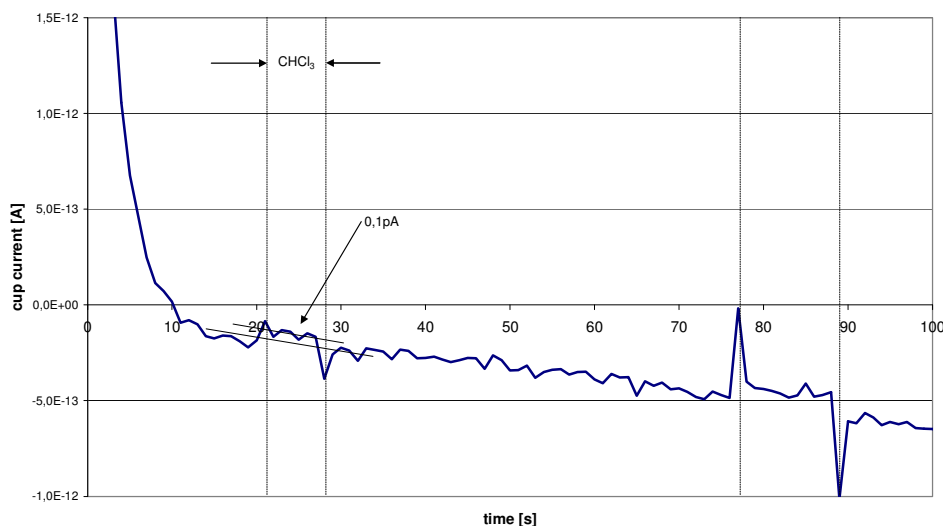


Fig. 4. Transient measurement of the cup current at 50V acceleration voltage by influx of chloroform (CHCl_3)

4. Summary

A suitable electron emissive material – LaB6 – was found for the here presented alternative soft ion source based on mechanism of photoelectron impact ionisation. LaB6 especially as a ceramic showed a suitable electron emission yield by ultraviolet radiation and was used for the investigation of gas ionisation under coupled photoelectron generation with acceleration in moderate electric fields. Several groups of molecules could be separated by simply varying voltages. Moreover, the idea of using LED sources for photo electron generation has been found useful, which, in combination with an MEMS arrangement will allow to go for higher ambient pressures.

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