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# Fabricating freely suspended structures optimized regarding mechanical and electrochemical stability for sensor applications

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A B S T R A C T

The concept of the micro-structured gas sensor discussed in this article promises the measurement of gas concentration and identification of gaseous substances in-situ. Furthermore it is fabricated exclusively using processes that are part of standard CMOS technology. In most MEMS devices a suspended structure is the main part of the sensor chip, realised using a wet etching sacrificial layer process. In this research we investigated the mechanical stability of different materials for the levitating structure and the electrochemical compatibility of the materials in the chip. A detailed analysis of the reactions of different material combinations in buffered oxide etch (BOE) revealed the occurrence of corrosion and hydrogen embrittlement in Al-ITO-$LaB_6$ systems. From there a new mechanism of hydrogen embrittlement in thin film layer systems with ITO was proposed. Finally we showed an optimized way of fabricating the sensor chip with prevention of corrosion and hydrogen embrittlement by galvanic isolation.



## 1. Introduction

The demand for microelectronic and micro-electro-mechanical systems (MEMS) is without question increasing rapidly. The interest in micro systems exceeds the application of accelerometers and pressure sensors, that are already part of every car or cell phone, by far [1,2]. Nowadays great efforts are made to replace as many elements as possible by micro structured devices. One large area of research concentrates on the development of sensors for gaseous substances, that are required in many parts of daily life for instance in areas of habitation or workplaces, for monitoring and regulation or in matter of human health and safety.

Recently, different concepts have been proposed for micro- or nano-structured gas detecting devices. Different types of MEMS resonant sensors that are able to detect specific gaseous substances in real time have been presented [3,4]. One approach to detect gases selectively is to use plasmonic resonances after exposing the sensor samples to a vapour flow at temperatures of 200°C to 400°C for 10 minutes [5]. Another chance to detect gaseous substances selectively in real-time is presented in [6], using molybdenum disulphide ($MoS_2$) thin-film transistors. The concept for the micro-structured gas sensor chip examined in this article offers the possibility to identify different gaseous substances and to measure their concentration in-situ. This is an important advantage over alternative sensor concepts as those are the requirements of many gas sensors systems operating in reality. Furthermore the sensor fabrication is only making use of standard planar technologies and there is no need for specific processes like exfoliation for instance.

The sensor concept originates from the idea of ionizing gaseous substances, collecting the generated ions and electrons and measure the response current. It is, for example, used in conventional photo ionization detectors (PID) where gases are ionized by photons from an ultraviolet (UV) ionization source, e.g. a discharge lamp [7]. Contrary to that, the concept of the sensor chip that is examined in this study uses electrons accelerated to a distinct kinetic energy for ionizing the gas molecules [8]. The principle of measuring gases using accelerated electrons is shown in Fig. 1. Electrons are emitted via photoeffect from a thin film of lanthanum hexaboride ($LaB_6$) and indium tin oxide (ITO) and are accelerated by the electric field of a grid electrode $U_{ac}$. After collisions with these electrons ionized gas molecules are collected by a cathode electrode ($U_{res}$). This causes a response current $I_{res}$ that indicates the gas molecule concentration as a function of the acceleration voltage $U_{ac}$. The adjustability of the electrons kinetic energy is the main advantage of ionization with electrons instead of photons, as molecules with different ionization potentials can be identified by varying the acceleration voltage.

For realising this sensor concept on a chip manufactured in planar technology a freely suspended grid is used to accelerate the photoelectrons that are emitted from an electron emitting layer. The design of a sensor chip like this is shown in Fig. 2. In general the chip is fabricated on a glass substrate that allows backside illumination of the electron

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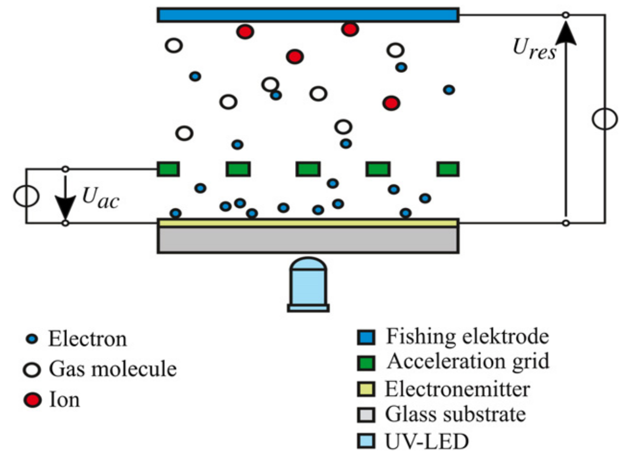


**Fig. 1.** Principle of gas measurement. Electrons ejected through a LED light beam are accelerated by the electric field of a grid electrode $U_{ac}$. Gas molecules ionized through collisions with these electrons are collected by a cathode electrode ($U_{res}$) and cause a response current ($I_{res}$).

emitting material. The suspended hexagonal grid with a minimum feature size of less than one micrometer is made of conductive materials. It is isolated from the electron emitting material by a layer of silicon dioxide ($SiO_2$) which is also used as sacrificial layer for the final suspension of the grid in a wet etching step.

Freely suspended structures are the major part of many MEMS devices. They can be found in common microphones as well as in concepts of recent research, for example in form of suspended narrow silicon nanowires [9,10]. In most techniques for fabricating freely suspended structures, wet etching plays an important role as it provides the isotropy and selectivity that is needed. Besides, restricted complexity of instrumentation, high throughput of wet etching steps and development and optimization over decades exhibits an important advantage over alternative technologies [11]. The suspended structures are predominantly fabricated by wet etching of a sacrificial layer, usually made of silicon dioxide, etched with buffered oxide etch (BOE).

Certainly classic materials like silicon, silicon dioxide and titanium nitride etc. are accompanied by a couple of more sophisticated materials like graphene, indium tin oxide or metal dichalcogenides to fulfil recent application demands. The embedding of new materials into well-known process sequences leads to challenges especially for structuring technologies. While there have been several studies about the behaviour of ITO in acids [12,13] and many available publications are dealing

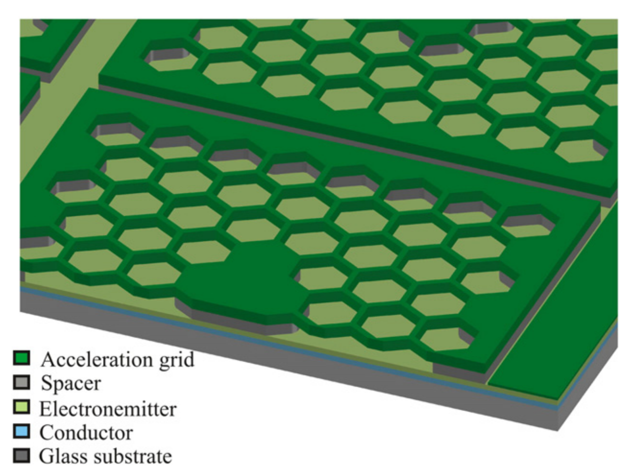


**Fig. 2.** Design of the gas detector chip. The electron emitting material is deposited on borosilicate glass substrate. Silicon dioxide, serving as spacer, isolates the honeycombed acceleration grid.

with the general properties of ITO, $LaB_6$ respectively $LaB_6$/ITO films [14–16], little is known about the behaviour of layer systems in wet etching procedures, in particular layer stacks made of ITO and $LaB_6$ during the fabrication of MEMS.

In this study we will describe the tests regarding mechanical and electrochemical compatibility of materials that are needed for the fabrication of the gas sensor chip. From the results of these tests a new mechanism of corrosion and hydrogen embrittlement of ITO in thin film systems during wet etching in BOE will be proposed. Finally the manufacturing of the sensor chip will be explained in detail. The results of all tests lead to a new process flow, compared to the process flow presented in previous studies, with replaced layer materials and additional sequences.

## 2. Experimental methods

In this section we will begin by describing the methods for studying the mechanical stability of suspended grids made of different materials. On one hand the material that is chosen to form the levitating part of the system has to fulfil certain electrical and mechanical properties, of course. On the other hand electrochemical properties of all materials that are used have to be taken into account as well wherever wet etching is applied. Hence we will look at the electrochemical compatibility of the materials present on the sensor chip.

### *2.1. Investigating mechanical stability*

From a mechanical point of view the stability of the freely suspended acceleration grid is the critical part of the sensor. In general the grid's layout is honeycombed, as this structure showed improved strength compared to former layouts. For further optimization of stability, application of alternative metals or metal stacks has been suggested previously [17]. Aluminum, chromium, titanium nitride and a stack made of titanium nitride and titanium were tested regarding their suitability for building levitating structures suspended by the use of hydrofluoric acid.

The choice of materials tested here is due to their mechanical properties. Young's modulus ranged from 68 GPa for aluminum to 248 GPa for titanium nitride and chromium. The stack made of a 200 nm thick layer titanium nitride on top of a 100 nm thick layer titanium is a combination of two materials with different values for Young's modulus, 248 GPa and 116 GPa, and similar values of about $9 \cdot 10^{-6} K^{-1}$ for the coefficient of linear thermal expansion. [18,19]

The samples were fabricated with different deposition and structuring methods. A 300 nm thick metal layer was deposited on silicon substrate coated with a 300 nm thick silicon dioxide. The material for the grids, made of aluminum, titanium and titanium nitride, were deposited by magnetron sputtering with argon (Ar), in case of titanium nitride with argon and nitrogen ($Ar/N_2$). The honeycombed grid structures were patterned by photolithography with MicroChemicals AZ 5214 E image reversal resist, processed in positive mode. As the minimum feature size of the grid is 800 nm, the photoresist was thinned by a factor of four to one in order to increase the resolution by decreasing the thickness of the photoresist. Aluminum, titanium nitride and the stack made of titanium and titanium nitride are structured utilizing reactive ion etching by chlorine gas ($Cl_2$), methane ($CH_4$) and silicon tetrachloride ($SiCl_4$) at 40 °C. Chromium was evaporated onto photolithographically patterned AZ 5214 E image reversal resist, thinned 4:1, processed in negative mode. The lift-off procedure was performed using acetone at 45°C supported by sonication. Subsequently buffered oxide etch (BOE) is used to remove the sacrificial layer made of silicon dioxide to realize the suspension of the grids.

Analysis was performed by taking scanning electron microscope (SEM) images. Cross section images of the samples, which were fractured right through the levitating structure, were taken to evaluate