Materials Science-Poland, 31(1), 2013, pp. 115-121
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-012-0075-3

Optical pH detector based on LTCC and sol-gel technologies*

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This paper presents an investigation on using sol-gel thin film as a material for sensors application in LTCC (Low Temperature Co-fired Ceramics) technology. This material gives the opportunity to make new, low-cost highly integrated optoelectronic devices. Sensors with optical detection are a significant part of these applications. They can be used for quick and safe diagnostics of some parameters. Authors present a pH detector with the optical detection system made of the LTCC material. The main part of the device is a flow channel with the chamber and sol-gel active material. The silica sol-gel with bromocresol green indicator was used. As the absorbance of sol-gel layer changes with the pH value of a measured medium, the transmitted light power was measured. The pH detector was integrated with the electronic components on the LTCC substrate.

Keywords: *Low Temperature Cofired Ceramics LTCC, sol-gel, pH sensor, optical amonia detection*

1. Introduction

For the last few years, an increase of the interest in optoelectronics microstructures has been observed. The world market for these products has grown rapidly and is likely to continue to be one of the most dynamic segments of the microelectronics. Structures, in which electrons are replaced by photons could be smaller, faster, more reliable and cheaper. Moreover, passive optical components could be integrated with electronic components or 3D microstructures like channels or reactors [1]. It especially makes possible to develop MEOMS (Micro Electro-Optical-Mechanical System) devices for medicine, lab-on-a-chip structures or for telecommunications, like optical switches [2–4]. Furthermore, the optoelectronics components could also be used in sensors for various measurements [5, 6].

Optical elements are mostly used in the sensors where detection is realized with light power measurement. In this kind of devices the light change *e.g.* power level or color, gives information about the measured parameter. This change may be caused by physical or chemical effects. One of the most popular is the measurement of absorption of the light transmitted through the active part of the sensors [7]. A change in the light transmission could inform about the changes in measured parameters. As an active element could be used either solid material or liquid with a special chemical indicator. Furthermore, in some cases, photoluminescence of the active material could be detected and measured [8].

However, there is still a need for materials which could be used in MOEMS devices. Especially in the group of ceramic microsystems, the currently used sensor materials allow us to provide detections for only some part of possible applications. Furthermore, they are often expensive and in many cases cannot operate at high temperatures (above 300 °C). For these reasons, the studies on new materials for ceramic MEOMS devices are needed. In this paper, authors present a detector made in LTCC and sol-gel techniques. Sol-gel materials have never been combined with ceramic materials for detector applications before. The presented work leads to achieving a completely new group of sol-gel materials. This would allow us to produce less expensive and smaller, highly integrated devices for many different applications.

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*This paper was presented at the 35th International Microelectronics and Packaging IMAPS-IEEE CPMT Poland Conference, 21 – 24 September 2011, Gdańsk-Sobieszewo, Poland

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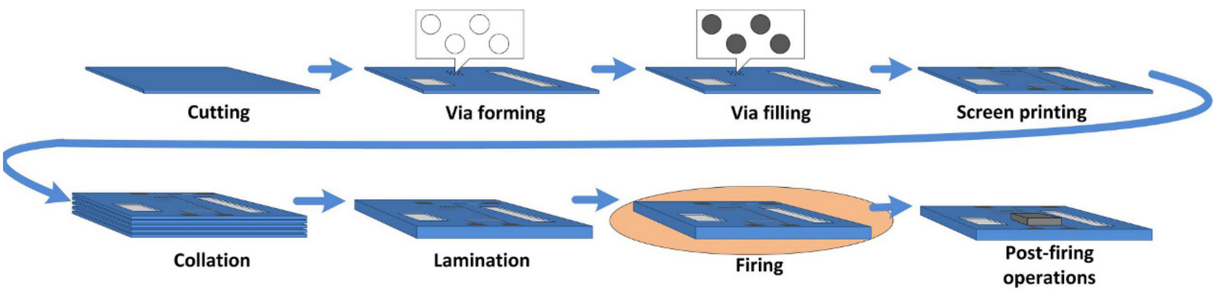

Fig. 1. Steps of the LTCC process.

This paper presents a detector for sensing ammonia or another liquid with high pH index. These liquid materials are often dangerous for human health, so they should be detected as quickly as possible. They could be produced as, for example, an unwanted result of chemical reaction. Protection against these substances in microfluidics devices, which could be realized by the presented sol-gel sensor-material, is very important. This kind of information could prevent damages or other problems in MEMS devices *e.g.* lab-on-chip.

Thanks to optical detection of the pH, the presented solution could be used in telemetric devices. In this case, the light signal to and from the device could be transmitted by the optical fibers even at a distance of a few kilometers. It allows supervising the detector from a large distance.

2. LTCC technology

Sensors based on optical detection could be made using thick film technology, especially ceramic materials. LTCC technology and ceramic materials are one of the most popular methods for producing microelectronic ceramic devices [9]. This technique is characterized by relatively simple technology and a possibility of creating 3D structures. It is a very good solution for ceramic MEMS. The sensors made in the LTCC technology are well known and often described. One of the biggest group of these devices are the sensors with optical detection.

The LTCC process uses, as a starting material, thin unfired glass/ceramics tape sheet. After cutting the sheets into the required shape (very often with a laser), the passive and dielectric components are made by screen printing method. If the structure is multilayered, then the interconnections through a single layer are made by vias, which are made of punched holes filled with silver paste. Separate layers are stacked, laminated and cofired to form a monolithic multilayer structure. The final step of this technology is firing in a temperature about 850 °C. The flow chart of this process is presented in Fig. 1.

The elements obtained in this process have all properties of standard ceramics. LTCC technique allows using these materials without problems and forming them in different, often complex shapes.

3. Sol-gel technology

Sol-gel technique is a chemical method of production of glass and ceramic materials from liquid phase. It is well know as a method for fabrication of thin optical layers with a wide range of properties. The name of this technology describes two states of material during processing. The first one is a colloidal suspension called sol, which is gelling and transforming into the material called gel, during the second stage [10].

Hydrolysis and alcoholic or water condensations of metal alkoxides are the main reactions proceeding in a sol-gel process (Fig. 2). The most popular aloxides for sol-gel thin layers preparation are the compounds containing silicon or titanium atoms. Usually, as a precursor of silica, tetramethoxysilane (TEOS) or tetramethoxysilane (TMOS) is used. To ensure proper reaction of sol, a catalyst is often used. Depending on material, it could be basic or acid (one of the most popular is hydrochloric acid). The last element of sol solution is a solvent *e.g.* ethyl alcohol.

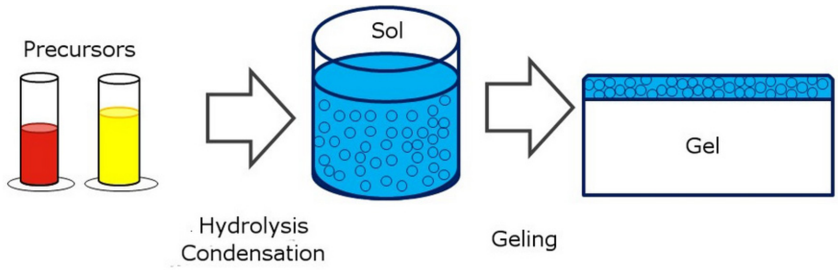

Fig. 2. Sol-gel process.

The parameters of the material could be very easily modified by the selection of precursor type and their quantity. For example the change of the quantity of titanium precursor allows one to obtain a material with refractive index of 1.4 to 2.3. Furthermore, doping of a sol with some chemical indicators is also possible. Such modified sol can interact with the outer factors like pH or humidity, which would give the opportunity to create various types of sensors [11]. A liquid consistence of sol allows coating the substrates by various techniques. The most popular ones are dip-coating and spin-coating methods.

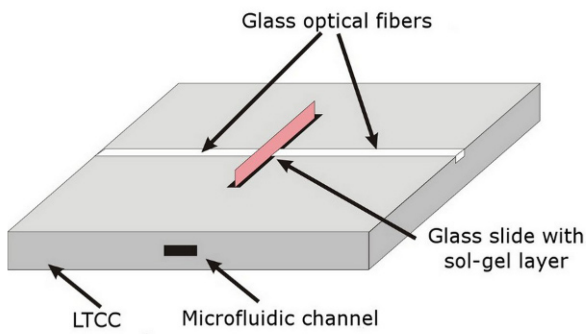

Fig. 3. Model of the detector.

4. Experiment

The presented detector was made using LTCC and sol-gel techniques. Up to now, sol-gel materials used as a sensor layer in ceramic substrates have never been reported.

The microfluidic channel for investigating a liquid flow was made inside the structure (Fig. 3). The width of this element was 1 mm. Over this channel, in its central part, 20 square holes of 200×200 μm size were made. These elements transferred the fumes from the flowing liquid to the thin glass (150 μm) covered with sol-gel layer. Thanks to that, the gaseous phase from the channel could be transported to the active sol-gel material. Size of the holes, glass slide thickness, liquid flow speed and method of placement were experimentally chosen to provide maximum measurement signal and sealing of the channel.

Sol-gel, which covered glass slide, contained a chemical indicator and the light absorption in this material depended on pH of the environment. On both sides of this glass slide, glass optical fibers with the dimension of 400 μm were placed in V-groves and fired with ceramics. These elements transmitted the light from the source to photodetector. The level of this signal was measured. The change in absorption on the glass with sol-gel layers, placed between these two fibers, gave information about the environment pH.

The main idea was not to integrate the glass with the ceramics permanently. Besides the fact that sol-gel reaction is reversible and after few hours the glass slide could be used for the second time, some parameters of the layer could be changed by the liquid flowing through the channel. Therefore, we used this element only once. Nevertheless, the glasses with sol-gel could be replaced and the sensors could be used many times. It is worth to mention that this disposable part is very cheap in production. Moreover, it is possible to use also a slide glass with different types of sol-gel material and indicators in this detector. The only condition, which should be fulfilled, is the change in light absorption during excitation. All these assumptions were taken into account during the experiments with sol-gel materials.

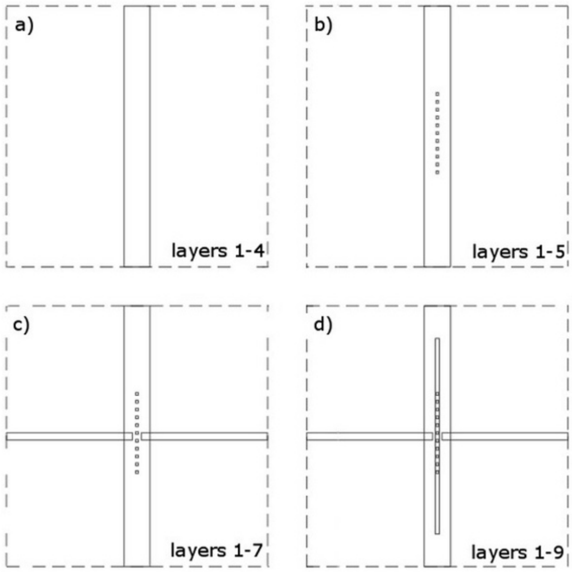

Fig. 4. Successive layers of LTCC material.

4.1. LTCC structure

The detector was made from the LTCC CeramTape GC. The structure consisted of nine layers of green tape material with a thickness equal to 360 μm before firing. Two first layers were not cut and they were used as substrates for the next layers. On the 3rd and 4th green tape layer, a microchannel was prepared. The width of this channel was 2 mm after firing of the material (Fig. 4a).

The 5th layer had small holes arranged in a line (Fig. 4b). These holes provided a way for the fumes of the liquid flowing through the device from the channel to the measuring chamber. The size of a single hole was 200 × 200 μm. The layers 6th to 9th were cut to obtain a rectangular chamber (0.2 mm width) for thin glass coated by sol-gel layer with pH indicator (Fig. 4c,d). Additionally, in the layers 6th and 7th two grooves for glass optical fiber were cut. Those elements were aligned with each other and orthogonal to the chamber provided for the glass coated with sol-gel layer.

All patterns were cut with a Nd:Yag laser. The layers were stacked together and laminated. The lamination was made in two steps at reduced pressure to prevent collapsing of the channel. The process time was 10 min and temperature 60 °C.

Glass optical fibers with 400 μm diameter were used for light transition. The polymer coating was removed from the fibers at high temperature. Before placing the fibers in the structure, their ends were polished to remove any irregularities after cutting. These elements were positioned under the optical microscope. The ends of the fibers were shifted from the edge. Taking into account the LTCC shrinkage during firing, an appropriate spacing was provided. The whole structure was fired in a chamber furnace with a temperature profile suitable for the used material.

4.2. Sol-gel material

Silica sol material was used as a basis for sensitive gel layers. The composition of this material was developed particularly for this application.

As precursors to silicon dioxide, tetraethyl orthosilicate (TEOS, Alfa Aesar) and phenyltriethoxysilane (PhTEOS, FLUKA) were used. During the experiments, also tetramethyl orthosilicate (TMOS) was tested. The first chemical compound was chosen because of the better quality of layers with thickness exceeding 400 μm. The thickness of the material was important because of higher absorption which could be easily detected with standard fotodiodes. The materials obtained with TMOS as a main precursor during the deposition on glass slides often had poor quality. They were cloudy and not transparent. For this reason, authors decided to use TEOS and PhTEOS (Fig. 5).

The materials were added to distilled water mixed with ethanol and stirred for 20 min at room temperature. After this time, 0.001 mol hydrochloric acid (HCl, POCH) was applied. It was used as a reaction catalyst. The whole solution was stirred for the next 40 min in 60 °C. The molar ratio of TMOS:PhTEOS in the prepared solution was 1:0.8.

During the first stage of the research, several chemical indicators were tested as pH sensitive additions. Moreover, during the tests, they were added at different technological stages. Thanks to that it was possible not only to recognize the best material, but also to learn the preparation procedure. These works allowed us to chose two chemical indicators

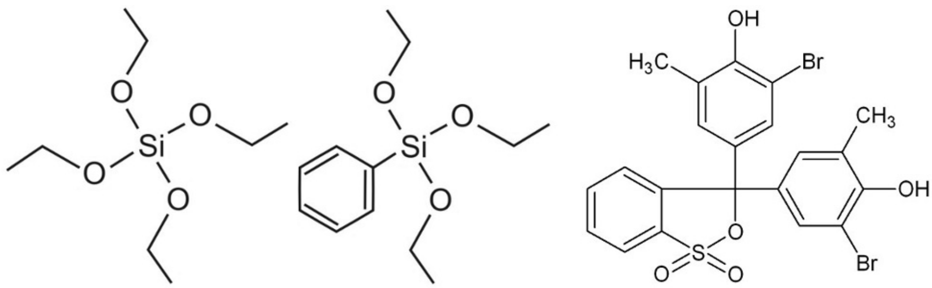

Fig. 5. Molecular structure of TEOS, PhTEOS and BG.

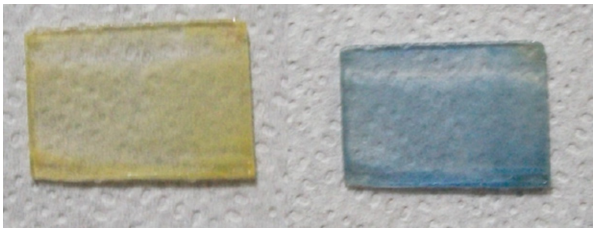

Fig. 6. Sol-gel layer on a glass slide in a neutral state and after stimulation in ammonia fumes.

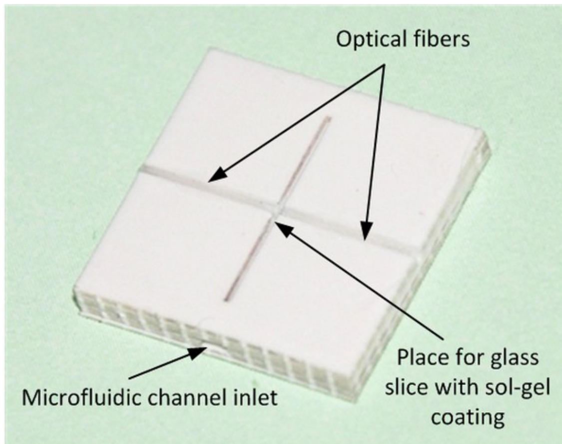

Fig. 7. Structure of pH detector.

for further tests – bromocresol green (BG) (POCH) and thymol blue (TB) (POCH), added after sol mixing. For these material and conditions, the obtained layers had the best quality.

The prepared solution was aged at room temperature for one day. After this time sol was deposited on the glass slide by dip coating method (Fig. 6). The procedure was carried with a dip-coater, controlled by the computer. The deposition speed was experimentally selected as 30 mm/sec. The slides were dried at 150 °C for 20 min.

The compound solution containing bromocresol green had a yellow color below pH 3.8 which changed to blue above pH 5.4. Between these two pH values, the material had intermediate color. Together with the color, material absorption changed. The experiments showed that the absorption in the prepared sol-gel material after exposure was on average by 10 % higher than in the non-exposed material. This level of changes could be easily detected by most types of detectors. Further works dedicated to these materials should yield a proper calibration curve for exposition level measurement.

5. Result and discussion

The quality of obtained materials was good. The size of a single detector was 15 × 15 mm. The channel was about 600 μm high and about 1.6 mm wide. Also the chamber provided for the glass with sol-gel layer had a proper width of about 180 μm. Proper size and shape of these elements are very important because it should provide very precise placing of the sol-gel layer. Also the buried glass optical fibers had good quality and were aligned orthogonal to the glass with the slide. The obtained structure is presented in Fig. 7.

The sol-gel material with chemical indicator was examined. The viscosity and density of the liquid were proper to use a dip-coating method for substrate covering. The speed of this operation was 30 mm/min. This parameter had an influence on the layer thickness. Faster coating resulted in thicker

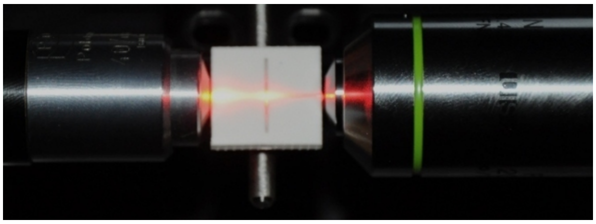

Fig. 8. Measurement set-up.

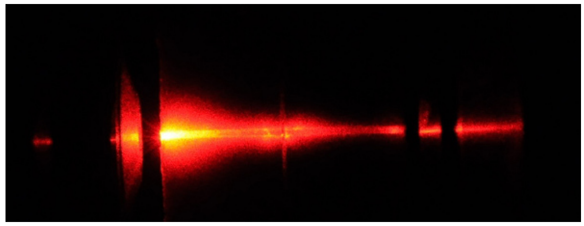

Fig. 9. Light transmission through glass optical fibers.

layers, but it was difficult to obtain a uniform layer. Furthermore, while the thickness was increasing, the light power attenuation in this layer was rising as well. The chosen coating speed was the best compromise between these effects. The thickness measured on the glass slide was 437 nm. For this thickness, the sol-gel layer was almost transparent. Moreover, the measured arithmetic roughness of the deposited material was as low as 7 nm. The value was not much higher than that of clean glass without any layer. It was very important because poor surface quality could cause high attenuation on the layer-air interface.

The experiments with light transmission through cofired optical fibers were made on the optical bench. As a light source, a He-Ne laser with the wavelength of 632 nm and 12 mW of optical power was used. Light was coupled to the fiber with 20× microscope objective. Also the 20× objective was used at the output. The measurement set-up for light coupling is presented in Fig. 7. The output signal level was measured with Si amplified photodetector from Thorlabs.

The results showed that the losses during transmission through the glass with sol-gel layer in the neutral environment were very small. They depended on the glass slide position and mismatch between two fibers. This value did not differ very much for different tested structures. The average was about 0.7 dB.

A part of the optical power was lost on the reflection from the glass surface. However, back reflection in the proposed configuration did not influence the sensors work. Because of the optical power loss, a suitable detector, especially with light power amplification should be used. This could allow detecting pH more precisely.

Table 1. Measurement results for different ammonia concentrations.

Aqua ammonia – water rate	U_1 [mV]	U_2 [mV]	Change [%]
100:0 %	60,23	54,21	9,9
75:25 %	59,12	53,84	8,9
50:50 %	62,98	55,32	12,1
25:75 %	60,12	54,12	9,9

U_1 – voltage measured in neutral state,
U_2 – voltage measured after stimulation.

The experiments were made for aqua ammonia with different concentrations. Ammonia was mixed with deionized water in 1:0.5, 1:1 and 0.5:1 ratios. The tests showed that the prepared sol-gel material was suitable for pH detection. As a result of the stimulation with aqua ammonia, its color changed from light yellow to dark blue.

Light transmission through the structure is presented in Fig. 8. In the middle part of the structure, scattering on the glass and sol-gel layer can be observed. The level of the signal was high enough to be seen with a naked eye (Fig. 9).

Some decrease in the signal power was observed with aqua ammonia solution flowing through the channel (Table 1).

The obtained results showed that the change in the signal level after the stimulation was of about 10 %. It is the value which could be easily detected. It would allow to use this structure as a detector for chemical materials with high pH index. The level of absorption in the sol-gel material did not change with ammonia concentration. The reason of this was the usage of bromocresol green as a chemical indicator. The limit value of pH for this material is 5.6 and for this value the material changes its color. All concentrations of ammonia used in this experiment had this index above this value, therefore the same absorption level was indicated by the detector. In the further works, the usage of phenolphthalein or thymolphthalein is planned. These compounds cause a change in the material absorption in pH range between 8 and 10.5. This would allow to detect different concentrations of ammonia.

6. Conclusion

In this paper, preliminary studies on optical pH sensors based on sol gel and LTTC technology have been presented. This is the first research on using sol-gel material in LTCC pH sensor. The results showed that it is possible to use silica sol-gel layer with an indicator deposited on glass slide for detection of the ammonia in a liquid flowing through the channel, but very important is the composition of the sol-gel material. The active material was placed on the separated glass without any permanent fixing, thus this chip could be used for many times. Moreover, the proposed construction allowed using glasses with different types of indicators. Thanks to that, the sensor could be used not only for pH measurement, but also for sensing different parameters. The obtained results are very promising and the work will be continued. This type of detection could be used *e.g.* as a part of a lab-on-a-chip system. Moreover, the structure and active part of the detector could be minimized to only several mm. In further studies, new indicators will be used and the integration of the light source and detector on one LTCC substrate is planned.

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Received: 2012-01-04
Accepted: 2012-12-04