

## Submicrosecond range surface heating and temperature measurement for efficient sensor reactivation

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### Abstract

A method for submicrosecond heating of sensor surfaces and simultaneous detection of the surface temperature was developed enabling accurate and fast reactivation of a semiconductor based oxygen sensor. High power electrical pulses with current densities of more than  $10^7$  A/cm<sup>2</sup> were applied to the 60-nm-thick Pt layer of a chemical semiconductor sensor structure resulting in surface temperatures as high as 700 K maintained in the nanosecond to microsecond range. Temperature measurement was carried out using the temperature dependent electrical resistance of the Pt film. Electrical power pulses of defined shape allowed accurate control of the surface temperature with ns time resolution. The high reactivation surface temperatures required high current densities, eventually leading to fatal destruction of the sensor structure. Comparative numerical simulations of the thermal impact as well as photo thermal and scanning force microscopy measurements were performed to optimize the heating process and to investigate the destruction mechanism. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Heat treatment; Platinum; Sensors

### 1. Introduction

The behaviour of chemical semiconductor sensors is mainly determined by the properties of the sensitive thin films, and surface pre-treatments are usually applied for improving response characteristics. Some chemical sensors are combined with an integrated electrical heater enabling higher operating temperatures, thus making use of the faster reaction dynamics at elevated temperatures [1,2].

We developed an all-solid state oxygen sensor (see Fig. 1) using the field effect in the semi-conducting part of an *n*-Si/SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/LaF<sub>3</sub>/Pt-structure [3]. The

sensor can be used for sensing oxygen concentrations in gases over five orders of magnitude with short response times and a Nernstian sensitivity of 58 mV/Δlg *p*<sub>O<sub>2</sub></sub>. Unfortunately, the response time of the sensor increases unacceptably even after few days use. A simple thermal treatment was found to be sufficient for reactivating the sensor [4], which can be repeated without limitation leading to a longer operating time. The thin Pt gate electrode (thickness 60 nm) of the sensor was used for electrical heating, and ms or even shorter heating pulses proved to be sufficient for reactivating the sensor. An electrical power of up to 1000 W corresponding to current densities in the order of  $10^7$  A/cm<sup>2</sup> had to be applied for 100 μs pulses, while the total energy was kept in the mJ range. The short heating pulses only heat the sensitive LaF<sub>3</sub>/Pt layer system, while the temperature rise inside the silicon

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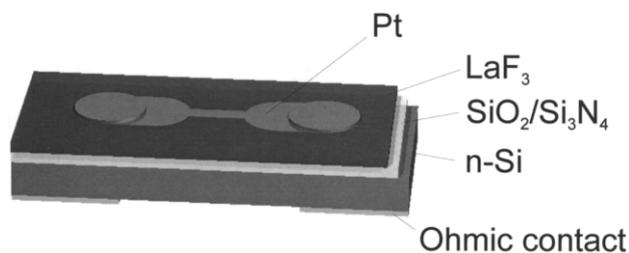


Fig. 1. Schematic of the thin-layer sensor structure.

substrate is comparatively small. The advantage of this is twofold. First, by localizing the thermal effects to the surface, only the sensitive layers, which require reactivation, are heated, and second, the small temperature rise of the substrate ensures rapid cooling. Therefore, the sensor remains at room temperature, and measurements can be continued immediately after reactivation. Heating of the substrate becomes more and more negligible for pulse lengths shorter than 100  $\mu$ s. The lack of accurate and sufficiently fast surface heating and temperature measurement techniques has so far hindered further investigations at times scales below 100  $\mu$ s. Furthermore, for fundamental investigations of the reactivation process a constant temperature plateau of a few hundred nanoseconds is preferable, but no method to achieve this conditions was accessible.

Therefore, the aim of the work reported here was to develop a surface temperature measurement method for the  $\mu$ s and sub  $\mu$ s range and to apply this technique to the improvement of the heating method to allow reactivation on a ns time scale. A computer simulation of the temperature distribution in the thin films for short heating pulses was performed using the CFD.ACE + software of CFD Research & Consulting Software GmbH. Since destruction of the Pt films was observed close to the conditions required for reactivation, the destruction process was investigated in detail by photo-thermal microscopy and atomic force microscopy (AFM). The remainder of the article is structured in the following manner. In Section 2, the technique for simultaneously heating and detecting the temperature is presented. Optimization of the reactivation process and investigation of the thin film destruction by numerical simulation and photo-thermal as well as atomic force microscopy is described in Section 3. Section 4 summarizes the results and gives a short outlook of the applicability of the developed method.

## 2. Heating of the sensor surface

Due to the lack of adequate methods, a technique for fast surface heating and simultaneous temperature measurements was developed. For this, the special structure of the oxygen sensor was utilized, which consisted of an *n*-Si/SiO<sub>2</sub> (60 nm)/Si<sub>3</sub>N<sub>4</sub> (80 nm) sub-

strate (5 × 10 mm) coated with a 240-nm-thick LaF<sub>3</sub> layer and a DC sputtered Pt film of 60 nm thickness and with dimensions of 0.5 × 1.5 mm<sup>2</sup> (see Fig. 1). The large areas on both sides were used as contact pads for electrical heating of the Pt film. High-current POGO contacts of Everett Charles Technologies formed the current input via copper strips. It is well known that the temperature dependence of the resistance of platinum wires or films can be used for accurate temperature measurements [5]. Therefore, the resistance of the platinum film was calculated from the current and the voltage measured during the electrical heating pulse applied to the Pt film. The voltage drop in the path region was obtained by performing a four-point resistance measurement at two needle shaped POGO contacts 1 mm apart, determining the resistance by directly measuring the heating current and the effective voltage. Hence, the task of the Pt film of the sensor structure is threefold. First, it serves as the gate electrode of the oxygen sensor as it was described in [3,4]. Second, it serves as a high-power heating element and, third, it is used as a surface temperature sensor.

As the resistance of the Pt films decreased by approximately 30–45% after heating the sample to temperatures higher than 200°C for the first time, all sensor structures were heated to 300°C for 30 s before use. The resistance and its temperature dependence were shown to be reproducible after this pre-treatment. Due to small variations in sample resistances, it was necessary to calibrate the resistance vs. temperature function for every sensor. A linear temperature dependence of the resistance was found for all 60-nm-thick Pt films. The resistance measured at room temperature was by a factor of 2.5–3 greater than the value for bulk material given in the literature. This is due to the different behaviour of thin film and bulk material and the roughness of the film resulting from the nm scale roughness of the underlying LaF<sub>3</sub> layer. For every sensor, a calibration was carried out at a minimum of two temperatures (room temperature and one value in the range 600–700 K) to get the individual temperature dependence of the resistance.

The quality of the electrical contacts is very important for heating at high power levels. Not only the high currents but also the resulting high temperatures were stressing the contacts. A polyimide-silver system EPO-TEK.P-1011 (Polytec, 76337 Waldborn, Germany) proved to be an excellent solution for the contact between the thin Pt film and a copper strip.

An example for an electrical heating experiment is given in Fig. 2. A constant voltage pulse was applied to the Pt film in this case. The resulting current decreased as the resistance of the Pt film increased with increasing temperature. Comparative experiments at much lower electrical power resulted in a stable current and a constant resistance. Therefore, the current and resis-

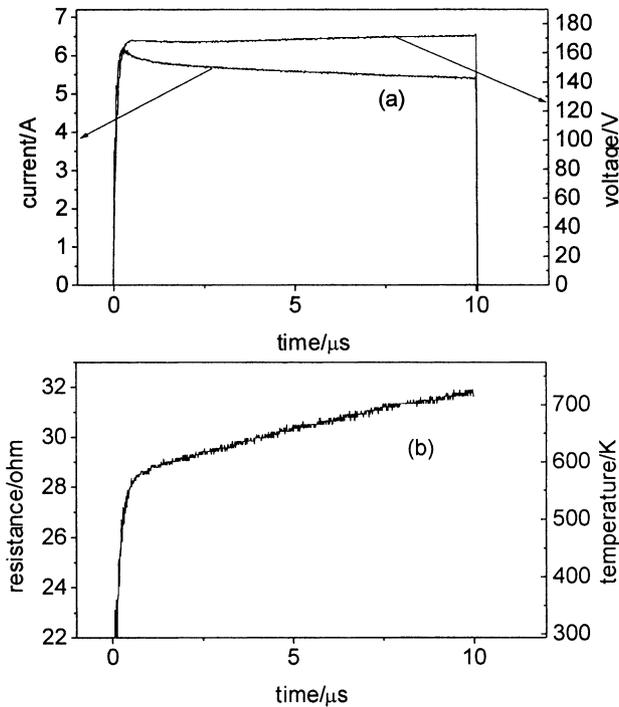


Fig. 2. Heating pulse of 10 μs applied to the structure shown in Fig. 1; (a) voltage and current; (b) resistance and surface temperature.

tance changes were in fact caused by the increasing temperature of the Pt. The change in resistance (left scale) and the calculated temperature (right scale) are given in Fig. 2b. As the voltage is switched to zero at the end of the pulse, the cooling of the structure following the pulse cannot be monitored. A measurement of the temperature decrease after the heating pulse is possible by applying low voltages leading to negligible Joule heating.

Instead of the continuous increase of temperature for the entire pulse length shown in Fig. 2b, a constant temperature plateau would be preferable for investigating and optimizing the reactivation process. To achieve this, appropriate combinations of resistances and capacitances in the power supply circuit were tested. Of course, this optimization had to be performed for every desired time range of the temperature plateau. An example for a typical pulse-forming system is given in Fig. 3. The capacitance C1 is charged before pulsing. When the switch S1 is closed the current is divided into two branches, i.e. a part of the current is flowing through the sensor resistance SR and the other part through R1 and C2. This avoids current spikes destroying the Pt film at the very beginning of the pulse. The RC element R1/C2 mainly determines the initial rate of temperature increase. The capacitance C3 ensures distribution of the total voltage drop between C1, SR and C3 for longer times. Therefore, the voltage drop across SR is not constant anymore. The resulting power vs. time and temperature vs. time curve for a heating

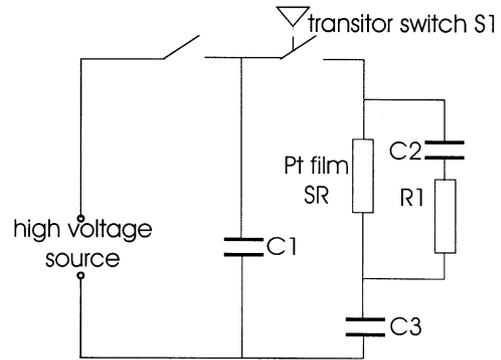


Fig. 3. Schematic of the power pulse forming circuit; values for the pulse shown in Fig. 4: C1 = 200 μF, C2 = 10 nF, R1 = 2 Ω, C3 = 110 nF, SR temperature dependent.

pulse of 1075 ns length is shown in Fig. 4 and Fig. 5, respectively. For the first 200 ns the temperature vs. time graph shows very large fluctuations, which correspond to a frequency of 25 MHz and are due to an initial shift between the current and voltage of some ns. We decided to optimize our system until the fluctuations occurred only during the first 200 ns, because we were interested in the final temperature and not in the initial temperature increase. For the experimental conditions shown, the temperature increases within 700 ns and then remains nearly constant for 310 ns in the range between 703 and 708 K. This temperature stability is suitable for the desired sensor reactivation. To reach this state, the rather extreme parameters given in Table 1 have to be used, illustrating the load on the 60-nm Pt film.

Although the power of this heating pulse and the resulting temperature of the Pt are very high, the assumption that all the energy would be dispersed in the Si bulk after the end of the heating predicts a temperature rise of the whole sensor element of only 0.025 K. This means that the sensor reaches room temperature within milliseconds after the heating impulse.

To prove the validity of this assumption, numerical simulations of the temperature distribution inside the structure using the CFD.ACE+ software were per-

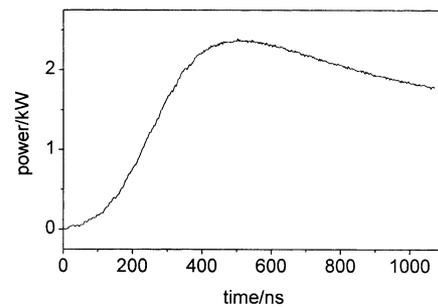


Fig. 4. Power/time profile for ns heating using the pulse forming circuit given in Fig. 3; pulse length 1075 ns.

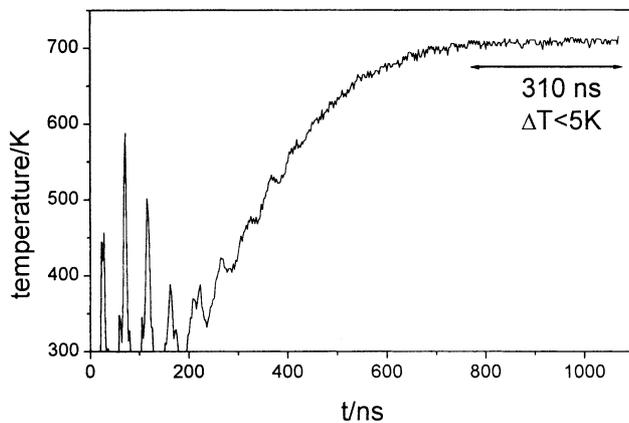


Fig. 5. Surface temperature for a heating pulse given in Fig. 4; the initial behaviour is not a real temperature oscillation but due to a shift between current and voltage for the first nanoseconds.

formed. To simplify the calculation, the constant power input and the heating time for a Pt film of  $(0.5 \times 1.5)$  mm<sup>2</sup> and 60 nm thickness were taken as the only parameters. For a heating period of 1 s at 10 W we found that the whole Si chip ( $5 \times 5 \times 0.5$  mm<sup>3</sup>) reaches temperatures higher than 370 K, while the Pt layer is at a temperature of 450 K, resulting in a temperature gradient over the entire sensor [6]. In contrast, short heating pulses in the 10  $\mu$ s or 10 ns range restricted the entire temperature gradient to the SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> layers, which have a low thermal conductivity (see Fig. 6), leaving the silicon substrate near room temperature. Therefore, only the Pt and the LaF<sub>3</sub> thin films are heated to high temperatures (e.g. 590 K for a 10  $\mu$ s 100 W pulse) and due to their high thermal conductivity both layers are nearly at the same temperature. The temperature rise inside the silicon substrate is very low, even at a distance of less than 1  $\mu$ m beneath the insulating layers the temperature is raised to only 340 K.

Therefore, the calculations proved our assumption and clearly showed that the thermal characteristic of the Si/SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/LaF<sub>3</sub>/Pt structure supports the short time high power electrical heating procedure. The combination of low thermal conductivity of the insulators and a high thermal conductivity for Pt and LaF<sub>3</sub> results in the desired behaviour of heating only the sensitive layers.

### 3. Mechanism of destruction

The electrical heating of the semiconductor structure

was limited by fatal destruction of the Pt film at temperatures in the range of 500–740 K. As this is the temperature range needed for efficient reactivation, careful investigation of this destruction process was needed.

Photo-thermal microscopy has been shown to be an advantageous tool for investigating electrically heated microstructures [7,8]. Photo-thermal microscopy at electrically heated structures is based on heating using alternating current to generate periodic temperature oscillations. In the present work this principle is applied to electrical heating the Pt film. The variation of the reflectivity of the same Pt film as a function of temperature is utilized for temperature measurements by detecting the reflected light of a HeNe laser, which is intensity modulated due to the variation of the reflectivity. Photo-thermal microscopy allows detection of local differences in surface temperature with a spatial resolution of approximately 1  $\mu$ m. Temperature differences might originate from lateral differences in the thermal conductivity of the film or from variations of the thermal contact to the substrate resulting in local variations of the perpendicular heat transport. A low thermal conductivity or an insufficient local adhesion could initiate local temperature spikes finally leading to the destruction of the film.

Photo-thermal investigations were performed on freshly prepared and destroyed samples as well as on samples stressed by electrical heating. A typical example for samples subjected to conditions close to destruction is given in Fig. 7. A comparison of the reflectivity and of the photo-thermal amplitude and phase shift reveals higher temperatures in small areas some  $\mu$ m in diameter. This might be due to hillocks or bubbles, where the film is delaminated from the substrate. The resulting local increase of surface temperature forms the initial stage of further destruction. Comparing the results obtained at freshly prepared samples and those with hillocks reveals that the hillocks are not correlated to inhomogeneities in thermal properties due to sample preparation, but were statistically distributed, ruling out problems in sample preparation as a reason for destruction.

Comparative AFM also confirmed the formation of hillocks as an initial stage of film destruction. Neither hillocks nor dispositions for hillocks were observed for freshly prepared samples or samples stressed at low electrical currents. A typical example for hillock formation after electrical heating is shown in Fig. 8. The

Table 1  
Parameters of the electrical heating pulse used in Fig. 4 and 5

Max. current (A)	Current density (A cm <sup>-2</sup> )	Max. voltage (V)	Max. power (W)	Total energy (J)
8.4	$2.8 \times 10^7$	293	2365	$1.82 \times 10^{-3}$

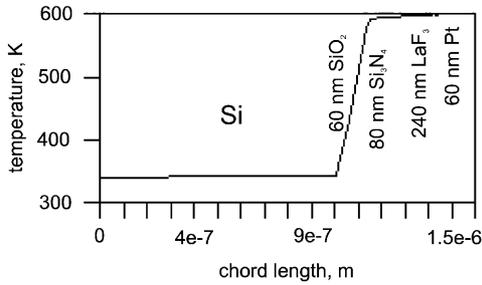


Fig. 6. Temperature profile of the surface region calculated for a heating power of 100 W and a 10  $\mu$ s pulse.

hillocks were found to have typical diameters of 0.5–2  $\mu$ m and a height between 200 and 400 nm.

An example for the next step in film destruction is shown in Fig. 9, where hillock formation and the result-

ing high temperature result in a hole in the Pt film. Once an irregularly shaped hole in the platinum film such as the bone shaped hole in Fig. 9 has formed, the temperature at the very edges is further increased due to increasing delamination at this location and higher current densities. This fact can easily be seen in Fig. 9, where a higher amplitude of the photo-thermal signal was observed at the ends of the bone shaped hole indicating elevated temperatures. Therefore, further destruction of the film perpendicular to the direction of current flow occurs, being additionally accelerated by the increased current density. Once the destruction process has started it continues immediately, making the observation of an intermediate state, as shown in Fig. 9, very unlikely.

In a final step of destruction, a lightning shaped

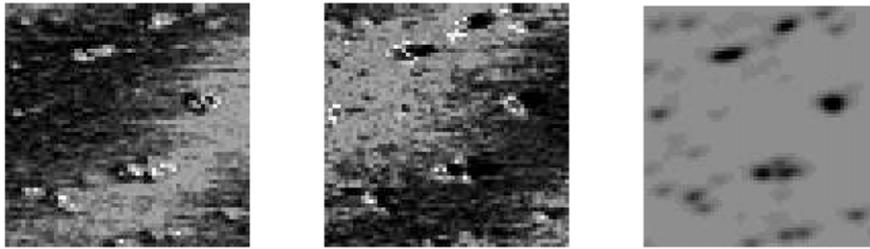


Fig. 7. Hillock formation, photo-thermal signal, left: amplitude, middle: phase shift; right: reflectivity (scale  $100 \times 100 \mu\text{m}^2$ ).

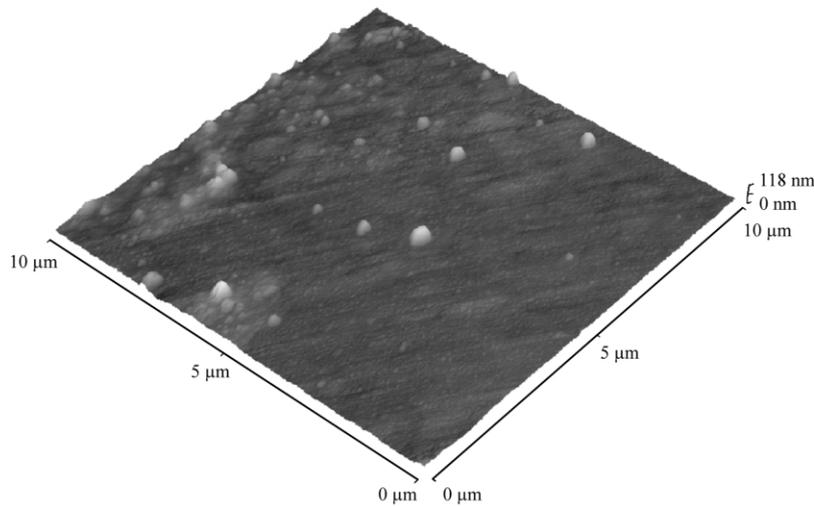


Fig. 8. AFM investigation of hillock formation after thermal stress.

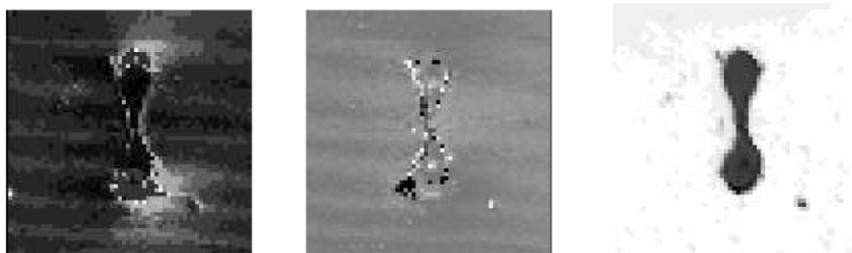


Fig. 9. Destruction of Pt film, photo-thermal signal, left: amplitude, middle: phase shift; right: reflectivity (scale  $200 \times 200 \mu\text{m}^2$ ).

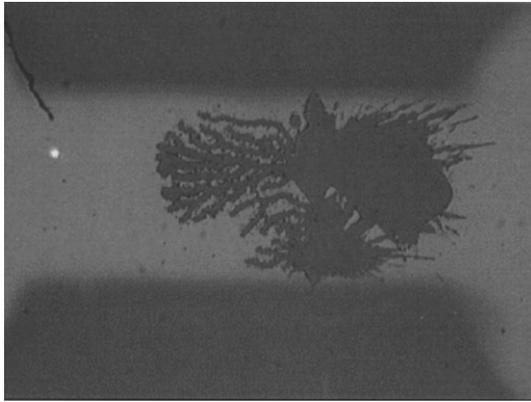


Fig. 10. Photograph of a destroyed Pt film (negative contact on the left).

structure across the film was observed. A photograph of this ultimate state is given in Fig. 10. The direction of this typical structure was determined by the direction of the current flow.

To further rule out problems in sample preparation as a reason for the destruction samples with and without  $\text{LaF}_3$  layer ( $\text{Si}/\text{SiO}_2/\text{Si}_3\text{N}_4/\text{LaF}_3/\text{Pt}$  or  $\text{Si}/\text{SiO}_2/\text{Si}_3\text{N}_4/\text{Pt}$ , respectively) were compared, resulting in the same destruction behaviour. Furthermore, comparative electrical heating experiments were also performed in vacuum. Again no significant increase in maximum current and temperature was found. Therefore, chemical reactions can also be excluded as reason for hillock formation and film destruction, which would be expected for inert, noble metals such as Pt.

Electro-migration might be another reason for hillock formation and destruction of conducting strips. To the best of our knowledge no investigations concerning Pt films have been reported in literature. However, for copper films, a destruction forced by electro-migration was reported at currents in the range of  $10^5 \text{ A cm}^{-2}$ – $10^6 \text{ A cm}^{-2}$  after several hours [9]. Mass depletion and mass accumulation during the course of electro-migration gives rise to voiding and hillock formation [10]. The stress time in our experiments is lower by several orders of magnitude, but the current density reached values of up to  $3 \times 10^7 \text{ A cm}^{-2}$ , and the higher temperature resulted in higher diffusion rates. The formation of hillocks and the high current density observed are supporting the hypothesis that electro-migration might be one reason for Pt film destruction in our experiments. However, the very short times compared to

electro-migration experiments reported in the literature makes this explanation doubtful.

#### 4. Conclusions

A method for thermal reactivation of a thin-film sensor element was achieved using very short electrical high-power pulses. The heating time can be reduced down to the ns range. For monitoring the reactivation process, a fast surface temperature measurement technique was developed using the temperature dependent resistance change of the Pt film. Accurate temperature control up to 730 K was achieved this way. Following a fast temperature rise a constant surface temperature can be achieved by appropriate modification of the electrical power supply. Using the Pt gate electrode as the heater allows accurate heating of the sensitive thin layer system to high temperatures, while the bulk of the silicon chip remains at room temperature. This allows fast and efficient reactivation of the sensor, making it a useful tool for long-term applications. The low energy consumption makes this reactivation advantageous for battery powered sensor systems.

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