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GAS SENSING WITH SURFACE-WAVE DEVICES[1]

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We have investigated a gas sensor based on a surface acoustic wave delay line coated with a selectively absorbing material. Coating materials were Palladium for the detection of hydrogen and the organic compound "Quadrol" with a specific sensitivity for SO_2. The variation of the velocity of sound associated with absorption by the layer allowed the detection of gas concentrations of the order of a few percent in the case of H_2 and of less than a ppm for SO_2 in air.

I. INTRODUCTION

In the past 15 years the application of Surface Acoustic Wave (SAW) devices has gained considerable importance for signal processing. Examples of such applications are filters, dellay lines, oscillators and convolvers. The reason for the importance of SAW devices for such purposes is the fact that, in contrast to bulk waves, the propagating surface wave is accessible to external perturbations at all times. Recently the potential of SAW devices for sensor purposes has called forth increasing attention (see, for example, [1—4]). For this application the influence of gases or liquids absorbed on the surface of the device is employed to propagate the surface wave. Selectivity and sensitivity of the sensor depend on the choice of suitable coatings of the surface of the device.

A surface layer on a SAW device will affect the propagation of the surface wave in several ways. Firstly its contribution to an effective elastic constant and to the mass density will modify the sound velocity. The relative variation of the sound velocity $\Delta v/v$ by a layer of thickness h is given by [5]

$$\frac{\Delta v}{v} = \frac{\omega k h}{4W}\left[4u_1^2 G_L - (u_1^2 + u_3^2)\, v_{RS\varrho L}^2\right] \qquad (1)$$

Here ω and k are frequency and wave vector of the surface wave, W its intensity and u_i the components of the displacement. v_{RS} is the SAW velocity of the substrate, G_L and ϱ_L are the shear module and the density of the layer, respectively. The sensitivity of the device is then given by the derivative of this expression with respect to ϱ_L and G_L, the relative importance of the two contributions depending on the layer material.

A second contribution to the sound velocity may exist if the substrate material is piezoelectric and if the sensor film changes its resistivity. Normally the electrical contribution to the potential energy of the wave will increase the sound velocity (piezoelectric stiffening) [5]. Shorting this field by a conducting layer will decrease sound velocity again by $\Delta v/v = -K^2/2$, where K is the piezoelectric coupling factor of the substrate material. In an intermediate regime of conductivity the electrical energy will relax with a time constant comparable to the inverse of the ultrasonic frequency. In this case we have a transition between the sound velocity of the open device and that of a metalcovered one. Although this effect is rather great, of the order of a few percent, its maximum sensitivity lies in a rather limited frequency- and conductivity regime. Therefore it has not been employed in our investigation.

Ultrasonic absorption can in principle be used for sensor purposes as well. Variations of, e.g., the viscosity of the layer will cause a corresponding change of the damping. This effect, however, is normally quite small and therefore difficult to detect. The electrical mechanism described above, on the other hand, can cause a very large absorption associated with a high sensitivity if the condition $\omega\tau = 1$ is reached. There remains, however the problem of reaching this regime under practical circumstances. Therefore we have restricted our technique to measuring changes of the velocity of propagation of the surface wave.

II. EXPERIMENTAL TECHNIQUE

The most simple technique to measure relative variations of the velocity of sound is to use the SAW device as the frequency determining element in an oscillator circuit. The change of sound velocity is then given by that of the frequency: $\Delta v/v = \Delta\omega/\omega$. In our apparatus we have employed a system consisting of two identical 6.9 μs delay lines on one $LiNbO_3$ chip operating at a centre frequency of 100 MHz (Fig. 1). This frequency was chosen as a compromise between the necessity to have high hk values to increase sensitivity (Eq. 1) and the simplicity construction of the SAW device and of the microwave components.

The oscillators were formed by connecting the tranducer pairs of each delay line by RF amplifiers and an adjustable attenuator to keep the loop gain close to one and to establish stable operation with a minimum of mode jumps. The outputs of the two oscillators were mixed and the difference frequency was

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measured by a frequency counter. This technique was used in order to suppress the influence of thermal expansion of the substrate. The frequency difference was recorded versus time.

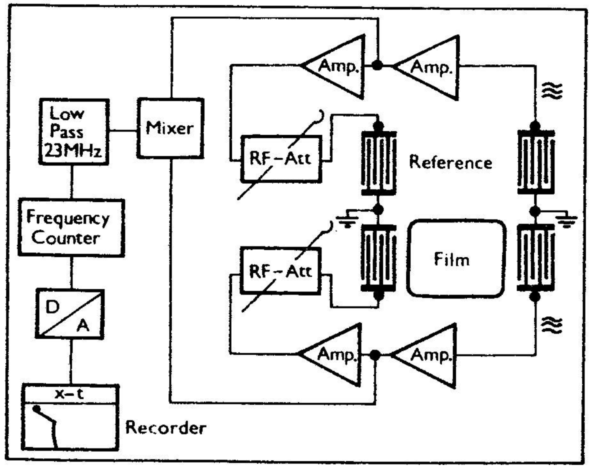

Fig. 1. Experimental setup for the measurement of small changes of sound velocity due to absorbed gases.

In spite of the differential technique there was still a considerable temperature dependence of the output frequency. Temperature therefore had to be stabilized carefuly within 10^{-2} K. This was achieved by heating either the copper block supporting the device or the gas flowing over it. The system was thermally insulated by mounting it into a dewar vessel. The operating temperature was kept slightly above room temperature at 26 °C.

The test gas was prepared by appropriately mixing synthetic air or nitrogen at a flow rate of 2 l/min with the gas to be sensed. The mixing ratio was controlled by calibrated gas flow regulators. Before admission of the test gas the system was evacuated in order to remove unwanted traces of other gases.

III. SAMPLE PREPARATION AND RESULTS

So far we have investigated two types of sensors. The first was produced by evaporating or sputtering a layer of Palladium onto one of the delay lines. Thickness ranged between 120 and 420 nm. In all cases a 10 nm layer of Cr was evaporated first to improve adhesion. Results for a sample with a sputtered Pd layer of 420 nm thickness are shown in Fig. 2.

From the measured curve it is obvious that the response of the device is rather slow. Furthermore it is to be characterized by at least two time constants. The first and relatively fast response it ascribed to an absorption forming Pd:H in the alpha phase [6] in which atomic hydrogen is dissolved homogeneously in the Pd matrix. The time constant for this process is determined by surface processes like dissociation of the H_2 molecule and its penetration into the bulk. After some time the (higher concentration-) beta phase begins to form in which the hydrogen in inhomogeneously distributed. Under our experimental conditions this happens at a lower time constant and over times exceeding the duration of the experiment. The time to reach half the final value in this experiment was roughly 5 h for the absorption process and 2.5 h for the desorption process. An improved response time of about 1 h could be achieved by sputtering a 20 nm layer of Platinum onto the Palladium surface. Obviously the catalytic action of Pt enhance the dissociation of the hydrogen molecule on the surface.

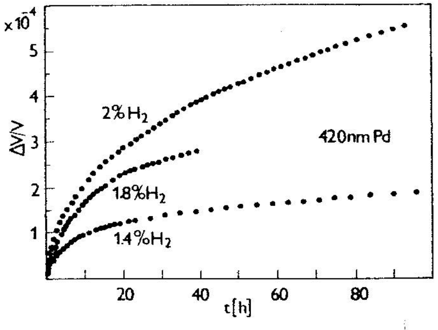

Fig. 2. Response of the Pd-coated device to three different hydrogen concentrations. Percentages in the figure are volume concentrations in air.

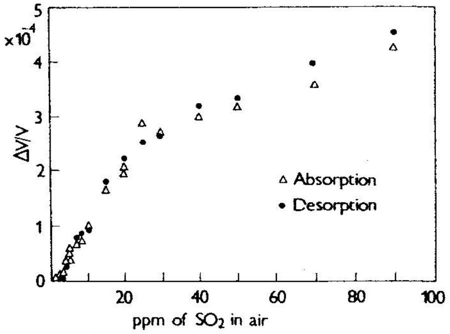

Fig. 3. Velocity change of the Quadrol — coated device for different SO_2 concentrations.

The second sensor material investigated was the organic compound Ethylenedinitrilotetra-2-propanol ('Quadrol'). This material can weakly (and thus reversibly) bind Lewis-acids like SO_2. At room temperature Quadrol is a highly viscous liquid, therefore only the mass variation associated with absorption wil influence sound velocity (second term in Eq. 1). It was applied to one of the delay lines by spin-coating the device with a solution of Quadrol in chloroform. The layer on the reference track was removed afterwards by immersing it into the solvent. The layer thus obtained had a thickness of about 0.5 µm.

In contrast to the Pd/H_2 sensor Quadrol has a very fast response for SO_2, the stationary state for absorption and desorption was reached after a few minutes. The sensitivity of the device is shown in Fig. 3 for concentrations between 0.05

and 90 ppm. At a concentration of 25 ppm we have a SO_2/Quadrol molar ratio of 1, the device begins to saturate and sensitivity decreases. The reason for the high sensitivity and the fast response is that Quadrol is a liquid and that the SO_2 molecule can thus diffuse into the bulk of the layer quite rapidly.

There are, however, a few problems with the use of this material. Firstly, the layer tends to peel off after some time, especially if there were dust particles on the device during preparation. With carefully prepared devices lifetimes exceeding 40 days couls be achieved. Another problem is the cross-sensitivity of Quadrol against other compounds like NO_2 and water vapour [7]. In fact Quadrol is so hydrophilic that a prolonged exposure to ambient air will destroy the film.

IV. CONCLUSION

We have investigated a gas-sensor based on a surface wave device coated with a thin layer of selectively absorbing sensor material. The absorption process is associated with a variation of the velocity of sound which can be easily measured by the frequency change of an oscillator circuit made with the SAW device.

Two types of sensor material were tested: Palladium with a specific sensitivity for hydrogen and Quadrol for sensing SO_2. The hydrogen sensor proved to work well in the concentration range of a few percent, but with very long response times. The SO_2 sensor was very sensitive and fast, concentrations of 0.05 ppm could be detected. The only problem encountered was the limited lifetime of the device.

For the future we plan firstly to improve the thermal stability of the device by using Quartz substrates instead of $LiNbO_3$. We intend to investigate the suitability of other organic sensor materials for the detection of other gases. Furthermore better materials and preparation methods must be found in order to improve the aging behaviour of the devices.

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ИНДИКАЦИЯ ГАЗА ПРИ ПОМОЩИ УСТРОЙСТВ, ОСНОВАННЫХ НА БАЗЕ ПОВЕРХНОСТНЫХ ВОЛН

Мы исследовали газовый индикатор, основанный на линии задержки акустической поверхностной волны, покрытой выборочно поглощающим материалом. Покрывающие материалы были палладий для детекции водорода и органическая смесь «Quadrol» со специфической чувствительностью по отношению к SO_2. Изменение скорости звука, связанное с поглощением слоя, позволяло детектировать концентрации газа порядка нескольких процентов в случае H_2 и меньше, чем ppm для SO_2 в воздухе.