February, 2005

Thin – Film Piezoelectric Acoustic Sensor (TFPAS): Further Experimental Validation of the Theory of Resonance Sensitivity.

L. M Dorozhkin
G N Dorozhkina
et al
Alexander G Sabelnikov

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Sensors and Actuators B 106 (2005) 529–533
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Thin-film piezoelectric acoustic sensor (TFPAS): further experimental validation of the theory of resonance sensitivity

L.M. Dorozhkin[a,*,1], G.N. Dorozhkina[b,2], A.V. Fokin[c], I.A. Rozanov[a], A.G. Sabelnikov[d], V.G. Sevastjanov[a]

[a] *N.S. Kurnakov Institute of General and Inorganic Chemistry, RAS, 31, Leninsky Prospect, GSP-1, 119991 Moscow, Russia*
[b] *State Scientific Center RF "NIOPIK", Moscow 103784, Russia*
[c] *N.N. Andreyev Acoustics Institute, Moscow 117036, Russia*
[d] *East Carolina University, Greenville, NC 27858-4353, USA*

Received 18 February 2004; received in revised form 18 June 2004; accepted 1 July 2004
Available online 19 February 2005

Abstract

The theory developed earlier, predicts that TFPAS sensitivity exhibits a periodic character, the period being equal to one half of the longitudinal acoustical wavelength in the sorption film material, λ_r. Sensitivity maxima occur at $l_r = (2n - 1)\lambda_r/4$, where n is 1, 2, 3, . . . and l_r is the sorption film thickness. Preliminary experiments showed that there was indeed a sharp increase in the sensitivity of TFPAS in the vicinity of $\lambda/4$ resonance. In this paper, $\lambda/4$ resonance is confirmed and the theory is further experimentally validated by observing another resonance at $3\lambda/4$. Potential applications of TFPAS operated at resonance frequencies for real-time detection and identification of chemical and biological weapons are discussed.

Keywords: Acoustic chemical sensor; Complex resonator; Sensitivity; Resonant increase

1. Introduction

Bulk acoustic wave sensors (e.g. quartz crystal microbalance, QCM) [1,2], surface acoustic wave (SAW) [3–6] sensors, etc., provide exceptional mass sensitivity by measuring shifts in resonant frequency. Such devices can be used both as chemical/gas [3–6], or biological [7] sensors, depending on the nature of a specific selective film that is deposited onto the device surface. Because the acoustic wave sensors are relatively inexpensive, readily available, and can provide high sensitivity with real-time detection and identification, they have the potential to become the method of choice for sensors operating at or near ambient conditions.

A while ago, a new type of acoustic sensor has been introduced that exploits the bulk longitudinal acoustic wave and has a complex resonator [8,9]. Its driving piezoelement was a thin piezoelectric film of several microns thickness that was deposited onto a non-piezoelectric substrate which played the role of a resonator cavity. The gas sorption film is applied onto the opposite side of the substrate.

The device was called thin film piezoelectric acoustic sensor (TFPAS). The TFPAS responds mainly to the changes in the thickness of the sorption layer, l_r; the latter is the most important parameter for the subsequent considerations.

The operating TFPAS frequency may lie within 70–1000 MHz region, but usually a frequency of 100 MHz is used. Unlike QCM, TFPAS operates at longitudinal, not a shear mode.

Similar to the other acoustic wave sensors, TFPAS sensitivity is defined as a derivative, $S = \mathrm{d}f_0/\mathrm{d}C$ where f_0 is the sensor working frequency and C is an analyte (gas) concentration.

* Corresponding author. Tel.: +7 95 9554871; fax: +7 95 9541279.
E-mail address: dorsens@igic.ras.ru (L.M. Dorozhkin).
[1] In some earlier papers spelled as Dorojkin.
[2] In some earlier papers spelled as Dorojkina.

0925-4005/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.snb.2004.07.021

Recently, it was shown theoretically that the sensitivity of TFPAS can be further substantially increased (two orders of magnitude and more) by the proper choice of the working frequency, resonator geometry, the acoustic parameters of the resonator elements such as density and sound velocity [10–11].

The theory predicted that TFPAS sensitivity would exhibit a periodic character, the period being equal to one half of the longitudinal acoustical wavelength in the sorption film material λ_r. Sensitivity maxima would occur at $l_r = (2n - 1)\lambda_r/4$; the corresponding minima would be shifted to $n\lambda_r/2$, where $n = 1, 2, 3, \ldots$ and l_r was defined earlier. Sensitivity peaks at $\lambda/4$, $3\lambda/4$, etc. were called resonances and n was named the resonance number. The results of preliminary experiments [11] showed that there was indeed a sharp increase in the sensitivity of TFPAS in the vicinity of $\lambda/4$ resonance.

In this paper, $\lambda/4$ resonance is confirmed and the theory is further experimentally validated by observing another resonance at $3\lambda/4$.

Potential applications of TFPAS operated at resonance frequencies for real-time detection and identification of chemical and biological weapons are discussed.

2. Theory

TFPAS operation principles and the theory of its resonance-like response were introduced in [10,11]. This theory resulted from the application of continuous acoustic wave (CW) analysis of TFPAS sensitivity mechanism. Here is the summary of the theory. TFPAS is treated as a complex, multilayer plane, one-dimensional, and nondamping resonator operating in an ambient analyzed gas.

The central equation that described the sensitivity dependence on the working TFPAS frequency, the relevant substrate and sorption layer material parameters, was:

$$S_l = \frac{1}{1 + \alpha(l_s c_r / l_r c_s)(\cos^2 k_r l_r + \alpha^{-2} \sin^2 k_r l_r)} \quad (1)$$

where S_l is the normalized sensitivity with respect to the sorption layer swelling and is proportional to the integrated, experimentally observed sensitivity, S; $\alpha = Z_s/Z_r$ is the ratio of the acoustic impedances of the substrate and the sorption film; c_s and c_r are the longitudinal sound velocity in the substrate material and the sorption layer, respectively; l_s is the substrate thickness; and k_r is the wave number.

The dependence of S_l on the sorption film thickness was shown to be of paramount importance. Since (1) is not illustrative and hard to treat, the numerical analysis was used. Calculations were made for three different, and commonly used substrate materials: fused quartz, Al–Y garnet (YAG), and sapphire. A vinyl-styrene copolymer (VSC) was used as the sorption film material.

Theoretically predicted dependence of S_l on (l_r/λ_r) is shown in Fig. 1. The parameters that were used for calculation are the same as in [11].

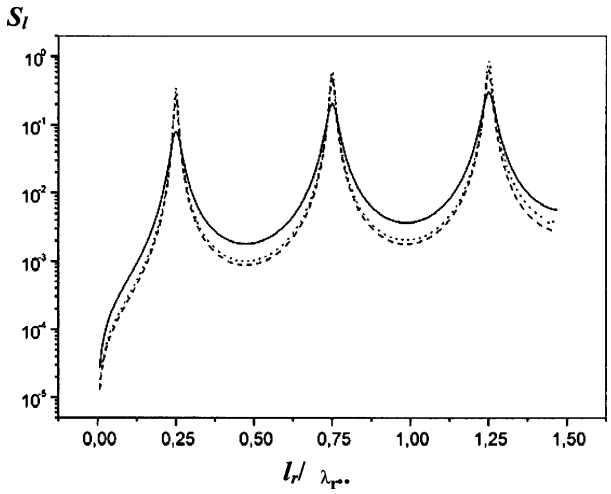

Fig. 1. Theoretical TFPAS sensitivity, S_l, versus l_r/λ_r.

It is clearly seen that there is a set of sensitivity maxima at $l_r = (2n - 1)\lambda_r/4$, and peak amplitudes grow up with the resonance number.

3. Experimental

The TFPAS design was described in detail elsewhere [8,9]. The sensor substrates were polished SiO_2 (fused) and YAG plates (1 1 1 cut) of 10 mm × 10 mm × 1.5 mm in size.

Commercially available vinyl-styrene copolymer was used as gas sensitive sorption film [10,11].

The VSC films were prepared by spin rotation (3500–4000 rpm for 1–2 min) of the polymer solution in toluene and/or chloroform. VSC concentrations were empirically chosen to provide the resultant film thickness of about 3.5 ± 1 and 11 ± 2 μm, corresponding to $\lambda/4$ and $3\lambda/4$ resonances. The thickness and the quality of the resultant films were examined with a Russian made commercial interference microscope. The accuracy of the l_r measurements was about 0.3 μm.

The *n*-decane was selected to use as an analyte because of convenience of its vapor preparation.

The experimental setup included a gas testing cell, a gas delivery system, and vapor generating cell all of which were described earlier in detail [10,11], read-out electronics, and data acquisition hardware/software. For the latter a laboratory made high-frequency, 100–120 MHz, amplifier of routine design was used. Its frequency could be adjusted to provide any desirable working mode. Short-time stability (15–20 min) was kept at the level of 10–20 Hz; long-time stability (up to 8 h) was 250–300 Hz. The typical frequency noise baseline is shown in Fig. 2.

Frequency changes were measured in real time with a standard frequency meter trivially interfaced with a PC that contained data acquisition software. The reference channel was not used in the experiments, because the short-time frequency stability was sufficient enough to obtain meaningful results.

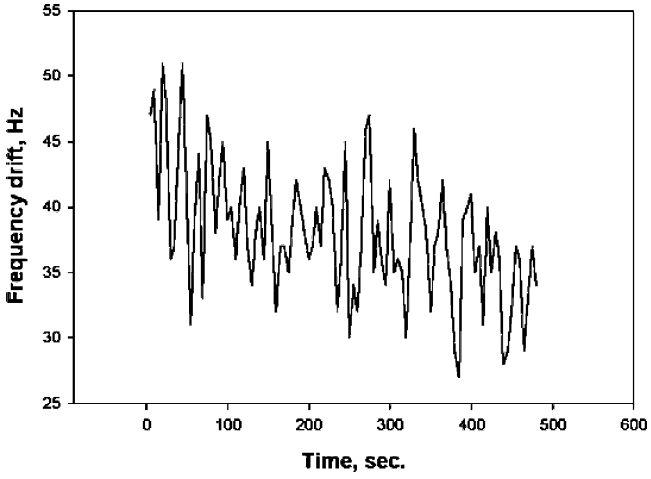

Fig. 2. TFPAS short time frequency stability.

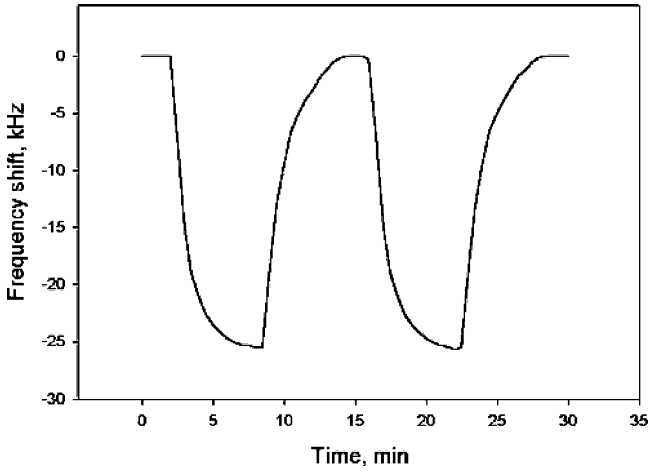

Fig. 3. TFPAS response (YAG substrate) to 100 ppm *n*-decane vapors under λ/4 peak resonance.

Analyte concentrations were determined from the amount of analyte evaporated during the experiment that was measured with the high precision Sartorius balances (10^{-5} g accuracy). The resultant gas concentration (in ppm) was calculated with the following formula:

$$C = \frac{t^0 \times 10^6}{273} \frac{\Delta P}{M v \tau}$$

where t^0 is the ambient air temperature (K), M the analyte molecular weight, v the air flow (l/min), and ΔP the weight in grams of the analyte evaporated.

In all the experiments C values were kept at the same level (100 ppm).

4. Results

Thin films for λ/4 experiments (3 μm thick) were smooth, transparent, and of easily controllable thickness. On the contrary, it was almost impossible to obtain thicker films (about 11 μm) of sufficient quality for 3λ/4 experiments by simply increasing the polymer concentration. After dozens of unsuccessful attempts we could find only one way to get what we wanted: by two consecutive applications of the same polymer solution onto the substrate. However, even with this procedure only a limited number of sensors of sufficient quality can be produced.

The typical TFPAS response (YAG substrate) to 100 ppm *n*-decane vapors under λ/4 peak resonance is shown in Fig. 3. It is seen that the response is reversible, symmetric, and repetitive.

The dependence of the TFPAS sensitivity on sorption film thickness is presented in Fig. 4A and B; solid lines are a theoretical prediction, filled circles are the experimental values. Both theoretical curves were normalized to the peak of the λ/4 resonance in case of fused quartz substrate.

Each experimental point is a mean among the series of gas experiments; the overall accuracy of the measurements was estimated to be 10–12% for λ/4 and 15–20% for 3λ/4 experiments. Lower accuracy of measurements for the latter was due to the poorer quality of the thick sorption films used (see above and Section 2).

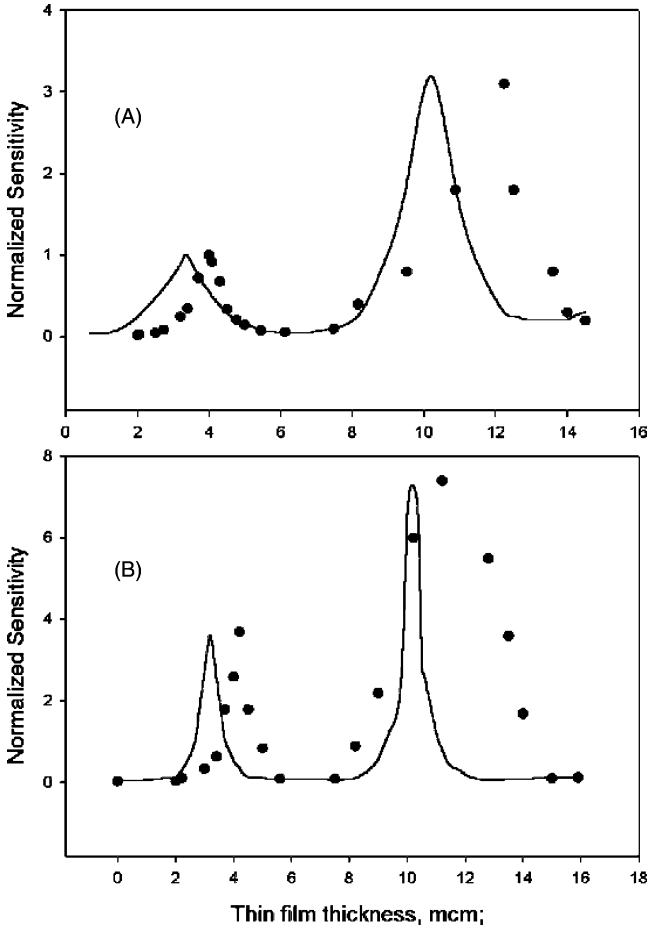

Fig. 4. Normalized (to 1/4 resonance of fused quartz substrate) TFPAS sensitivity: (A) fused quartz substrate and (B) YAG substrate.

5. Discussion

Several issues will be discussed here. First, there is a good agreement between theoretically predicted and experimentally obtained curves of S_l versus l_r (Fig. 4A and B). Slightly shifted positions of the experimental peaks versus those predicted theoretically may be explained by the fact that for theoretical prediction the longitudinal sound velocity of rubber (substance close to VSC) was used. These results indicate that the theory of resonant sensitivity of the acoustic waves sensors [11] that was developed on the basis of continuous waves analysis approach is valid.

It may be expected that the theory is fully applicable to the other bulk acoustic wave sensors. However, quarts crystal microbalance (QCM) was not a "suitable case for resonant sensitivity increase" [11]. As more thorough considerations show, this may be true only for QCM with rather low working frequencies (10 MHz or lower). For QCM with higher working frequencies resonance-like enhancement of sensitivity may be expected. It is conceivable, that under "non-resonant conditions", the increase in the sensitivity of QCM may be achieved by employing high odd harmonics (third, fifth, seventh, etc.) [12]. For instance, a QCM operating at 49MHz (that is about 25 more sensitive than a 10 MHz device) the sound wavelength in most sorption materials would be about 20 μm. So, the additional, λ/4 resonance sensitivity increase would be expected at the sorption film thickness of 5 μm, which seems feasible. If this turns out to be true, the scope of QCM applications may be substantially extended. Experiments are underway to validate this expectations.

Returning to TFPAS, it would be interesting to estimate detection limit (Δl_r) in measurements of l_r at resonant maxima. It can be easily done by substituting typical values for symbols in the known equation for sensitivity [11]:

$$S_l = -\frac{l_r}{f_0}\frac{df_0}{dl_r} \quad \text{(where } f_0 \text{ is operational frequency)} \qquad (2)$$

with $S_l \sim 0.3$–0.5 (from theoretical curves in Fig. 1), $l_r \sim 3\,\mu m$, $f_0 \sim 10^8$ Hz, df_0 (feasible frequency drift) ~ 10 Hz. That gives the values for Δl_r of ~0.01 Å.

Such a high detection limit (sensitivity) opens up the possibility of a wide practical application of the sensor. It is feasible to use the resonance-like character for building a supersensitive (ppb and ppt range) gas sensors with many applications. One of them might be a sensor for detection of buried mines and ordnance, another for detection and identification of chemical warfare agents. TFPAS adapted to a liquid media might be used for real-time measurements of biological and toxic agents in water. The latter becomes of special concern, because of the possibility of detection of biowarfare agents.

Taking into account the detection limit of measurements of Δl_r estimated above, and assuming that highly specific antibodies are attached to a sorption film, the maximal expected sensitivity of the sensor towards biowarfare agents (bacterial cells and virus particles) could be estimated. In order to do that, we should calculate the number of cells that would fit into the space (over the sensor film) with the volume determined by the product: thickness detection limit (0.01 Å) × sensor active surface area (0.1 cm^2) = 10^{-11} cm^3. The volume of an average bacterial cell, a rod of 2 μm long and 1 μm in diameter, is about 10^{-12} cm^3. Thus, the expected sensitivity for bacteria is just 10 cells and is higher than with PCR-based sensors [13]. The number of viruses, though, that might be detected is significantly higher: for instance, only about 620 particles of a smallpox virus (400 nm × 200 nm × 200 nm). Nevertheless, it is still one of the highest for viruses.

6. Conclusions

In this paper we confirm TFPAS λ/4 resonance sensitivity increase that was observed in preliminary experiments earlier. The theory of resonance sensitivity is further experimentally validated by observing another resonance at 3λ/4.

The estimated detection limit (Δl_r) in measurements of l_r at resonant maxima is of the order 0.01 Å. Such a high detection limit (sensitivity) opens up the possibility of a wide practical application of the sensor, including detection of chemical and biological warfare agents. Estimated sensitivity for the latter is about 10 bacterial cells, and about 600 virions (for smallpox virus).

It is suggested that the resonance-like enhancement of sensitivity of QCM, another bulk acoustic wave sensor may be easily achieved by the appropriate increase of the thickness of a sorption film. That would substantially extend the scope of QCM applications.

Acknowledgements

We thank Dr. V. Boritko and Dr. A. Lavrenov for their assistance in some experiments, and Dr. V. Volkov (Brookhaven National Laboratory, USA) for useful and stimulating discussions.

References

[1] W. King, Piezoelectric sorption detector, Anal. Chem. 36 (1964) 1735–1739.
[2] W. King, Using quartz crystals as sorption detectors, Res. Dev. 120 (1969) 28–34.
[3] D.S. Ballantine, R.M. White, S.J. Martin, A.J. Ricco, E.T. Zellers, G.C. Frye, H. Woltjen, Acoustic Wave Sensors: Theory, Design, and Physico-Chemical Applications, Academic Press, New York, 1977.
[4] J. Grate, S. Martin, R. White, Acoustic Wave Microsensors, Part I, Anal. Chem. 65 (1993) 940A–948A.
[5] J.W. Grate, S.J. Martin, R.M. White, Acoustic Wave Microsensors, Part II, Anal. Chem. 65 (1993) 987A–996A.
[6] L.M. Dorozhkin, I.A. Rozanov, The acoustic wave chemical gas sensors, Russ. J. Anal. Chem. 56 (2001) 455–474 (a review).
[7] D. Diamond (Ed.), Principles of Chemical and Biological Sensors, Wiley, New York, 1998.

[8] L.M. Dorojkine, V.V. Volkov, V.S. Doroshenko, A.A. Lavrenov, D.A. Mourashov, I.A. Rozanov, Thin-film piezoelectric acoustic sensors. Application to the detection of hydrocarbons, Sens. Actuators B 44 (1997) 488–494.
[9] L.M. Dorojkine, V.S. Doroshenko, V.A. Kezko, Yu.I. Krasilov, N.T. Kuznetsov, D.A. Mourasov, I.A. Rozanov, V.F. Rjurikov, A.A. Lavrenov, The sensitive element for gas analysis, Russian Patent No. 2060497 (1993).
[10] L.M. Dorojkine, S.V. Boritko, G.N. Dorojkina, A.V. Fokin, I.A. Rozanov, The resonant-like behavior of the acoustic wave chemical gas sensors, Russ. J. Anal. Chem. 55 (2000) 138–143.
[11] L.M. Dorojkine, S.V. Boritko, G.N. Dorojkina, A.V. Fokin, I.A. Rozanov, The resonant character of the sensitivity of the acoustic wave sensors, Sens. Actuators B 89 (2003) 15–20.
[12] R. Lucklum, P. Hauptmann, Determination of polymer shear modulus with quartz crystal resonators, Faraday Discuss. 107 (1997) 123–140.
[13] T.W. Graham, A. Sabelnikov, How much is enough: real-time detection and identification of biological weapon agents, J. Homeland Security Emergency Manage. 1 (2004) (Article 303).