Ultrasensitive wireless QCM bio/gas sensors

Hirotsugu Ogi (Graduate School of Engineering, Osaka University)

1. Introduction

 α -quartz is a transparent piezoelectric material which exhibits 32-point-group symmetry, showing six independent elastic constants, two independent piezoelectric constants, and two independent dielectric constants. It has long been used as a massdetecting sensor material because of its low material cost, low mass density (2650 kg/m³), high *Q*-value of vibration, and extremely high temperature stability of resonance modes in certain crystal orientations.

When a target material is attached to the surface of the quartz-crystal resonator, its resonance frequency decreases due to the increase in the effective mass of the resonator system. This mechanism can be used as the label-free biosensor. The resonance frequency changes when the shape of the resonator is changed by an external force. Using this phenomenon, it can be used as a stress (strain) sensor. A change in the resonator temperature varies the elastic constants of the resonator material, which changes the resonant frequency, making it a temperature sensor. Using a bilayer resonator with thermal-expansion coefficients, different the temperature change causes the bending deformation of the resonator, which also changes the resonant frequency. Furthermore, when a film sensitive to a specific gas is deposited on the surface of the resonator and the target gas is adsorbed, not only an increase in the mass but also a change in shape due to the generation of the traction force occur, and the resonance frequency changes. This principle can be used as a gas sensor. Thus, the QCM sensor can be utilized for sensing various physical and chemical targets (Fig. 1).

In these sensing principles, the common key parameter that governs their sensitivity is the

"thinness" of the resonator. The thinner (i.e., lighter) the resonator, the greater the change in resonance frequency due to the relative increase in the mass of the adsorbed target, resulting in the greater the sensitivity. The thinner the resonator, the more easily it bends and undergoes shape changes, which also increases the amount of change in the resonance frequency. However, existing QCM sensors require heavy metallic electrodes and wiring to connect them to both sides of the resonator, and furthermore, the resonator itself is required to be strong enough to withstand liquid pressure and atmospheric pressure, and it has been difficult to make the resonator thinner.

The author has developed the wirelesselectrodeless QCM (WE-QCM) sensors,¹⁻⁴⁾ where the electromagnetic (EM) wave is used for generating and detecting the vibration of the quartz resonator contactlessly. Then, by introducing a proprietary MEMS process, the resonator can be made even thinner and QCM sensor chips can be mass-produced.⁵⁻⁷⁾ The thinner resonator increases the measurement frequency, enabling battery-free wireless experiments at distances of 10 meters or more.⁸⁾

This paper gives belief overview of the mechanism of WE-QCM sensors and their applications.

2. Antenna-based wireless QCM measurements

The WE-QCM uses antennas instead of electrodes. A typical measurement setup is illustrated in Fig. 2. A tone burst signal with a frequency close to the mechanical resonance frequency of the resonator is applied to the antenna for excitation. The EM wave causes the mechanical vibration of the quartz resonator via the converse piezoelectric effect. The mechanical vibration continues for a while after



Fig. 1 Various mechanisms for changing resonance frequency of a resonator.



Fig. 2 Setup of a wireless-electrodeless QCM.

the excitation, launching the EM wave due to the piezoelectric effect. This can be detected by the other antenna for detection, allowing the non-contact measurement of the resonance frequency of the resonator. This measurement configuration offers the following important advantages. (i) Because the resonator is completely isolated, it can be be packaged inside a microchannel. (ii) The detection sensitivity can be significantly improved because of the electrodeless characteristic. (iii) Thinning of the resonator increases the operating frequency up to VHF and UHF bands, enabling remote and batteryfree measurements beyond 10 meters.

3. Applications to bio/gas sensors

The WE-QCM allowed biosensing experiments with much higher fundamental resonance frequencies (~ 180 MHz), compared with previous QCM biosensors, resulting in much higher sensitivity.^{3,9)} Multichannel measurements are made possible by exciting many quartz resonators simultaneously by one set of antennas (Fig. 3).¹⁰⁾ Thanks to its high-frequency measurement, the WE-QCM is suitable for evaluating the viscoelasticity of the formed protein layer.¹¹⁻¹³⁾ Furthermore, it has been used for studies on aggregation reactions of amyloidogenic proteins.¹⁴⁻¹⁶⁾

By depositing Pd-based alloy film on the surface of the quartz resonator, the WE-QCM operates as a hydrogen-gas sensor. ¹⁷⁻¹⁹ The detection mechanism in this case relies on the bending deformation of the resonator rather than the mass loading effect. This was confirmed by the fact that the amount of the frequency change was larger when the Pd-based alloy thin film was deposited on one side than when it was deposited on both sides.¹⁷⁾

4. Future prospects

Because the WE-QCM contributes not only to ultrasensitive detection of bio/gas molecules but also to long-range remote sensing that requires no power supply on the sensor side (Fig. 4), it enables a semipermanent gas sensing in inaccessible area and semipermanent stress measurement inside infrastructures by embedded the sensor chip in concrete.







Fig. 4 Battery-free long-range wireless sensing.

References

- 1) H. Ogi *et al.*, Anal. Chem. **78**, 6903 (2006).
- H. Ogi *et al.*, Biosens. Bioelectron. 22, 3238 (2007).
- 3) H. Ogi *et al.*, Anal. Chem. **81**, 8068 (2009).
- 4) H. Ogi et al., Biosen. Bioelectron. **26**, 4819 (2011).
- 5) F. Kato *et al.*, Jpn. J. Appl. Phys. **50**, 07HD03 (2011).
- 6) F. Kato *et al.*, Biosen. Bioelectron. **33**, 139 (2012).
- 7) L. Zhou *et al.*, Anal. Chem. **95**, 5507 (2023).
- 8) Kanto *et al.*, Proc. Symp. Ultrason. Electron. **43**, 1Pa3-5 (2022).
- 9) H. Ogi *et al.*, Biosen. Bioelectron. **26**, 4819 (2011).
- 10) H. Ogi et al., Anal. Chem. 82, 3957 (2010).
- 11) T. Shagawa *et al.*, Jpn. J. Appl. Phys. **54**, 096601 (2015).
- 12) Y.-T. Lai et al., Langmuir 34, 5474 (2018).
- 13) K. Noi *et al.*, Jpn. J. Appl. Phys. **59**, SKKB03 (2020).
- 14) K. Noi et al., Anal. Chem. 93, 11176 (2021).
- 15) K. Nakajima *et al.*, Nat. Commun. **13**, 5689 (2022).
- 16) L. Zhou et al., ACS Sensors 8, 2598 (2023).
- 17) L. Zhou *et al.*, Appl. Phys. Lett. **115**, 171901 (2019).
- L. Zhou *et al.*, Sens. Actuat. B. **334**, 129651 (2021).
- 19) F. Kato *et al.*, Jpn. J. Appl. Phys., **61** 126501 (2022).