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An Efficient Piezoelectric Analysis for Quartz Crystal Nanobalance Gas Sensor

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Abstract: This paper presents an efficient scheme to design the most used biosensor Quartz crystal nanobalance (QCN). The main characteristic of QCN is very mass sensitivity. It means a little variation of deposited mass on the surface of QCN and it will cause the change of thickness-shear-mode resonant frequency. An electro-mechanical coupled-field 3D finite element method is applied to analyze the resonant frequency, modal shape, harmonic response, and the contour effect for AT-cut piezoelectric quartz crystal (PQC). Finally, the application of QCN as gas sensor is illustrated and studied in detail. All the simulated results indicate well compared to the theoretical values and experimental results.

Keywords: piezoelectric quartz crystal (PQC); Quartz crystal nanobalance (QCN); Finite element method (FEM); electro-mechanical coupled field; thickness-shear-mode (TSM)

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1. Introduction

The piezoelectric quartz crystal resonator has been widely used as mass sensitive detector in electrochemical experiments recently. The resonant frequency of thickness-shear-mode was affected by the small mass loading on AT-cut quartz plate with electrodes film. It was shown theoretically from well-known Sauerbrey equation [1]. Applying the vibration theory of piezoelectric quartz crystal (PQC) on the development of biosensor, such as the detection of bacteria, immunoglobulin and the identification of environmental gas and liquid [2-5], is the fashion in recent years. The main reason is PQC has high sensitivity for the variation of mass. About the piezoelectricity of PQC is an alternating electrical field applied perpendicular to its surface results in the generation of mechanical vibrations [6]. In dependence on the physical characteristic of mechanical vibration, different devices of PQC biosensor can be distinguished: surface acoustic wave (SAW), thickness shear mode (TSM), flexural plate wave (FPW) and acoustic plate mode (APM) devices. Compared to TSM devices, SAW, FPW and APM devices have higher mass sensitivity, but they are not suitable for the application in liquid media because of their high damping [7]. Furthermore, among these acoustic sensors, TSM devices have the lowest temperature dependence of resonant frequency and often used as QCN. In this article, QCN have been investigated.

Generally speaking, QCN consists of a thin AT-cut quartz disk with metal electrodes deposited on both sides of quartz surfaces. After deposition of different sensitive membrane on the surface of the AT-cut quartz disk, QCN is widely applied in many fields of biochemical analysis. However, the design and development of QCN is usually done by experiments in the past. It is hard to avoid having error between the experimental results and true physical phenomenon of QCN because of operative error or improper apparatus and easily results in the failure of development of QCN. Therefore, applying 2D FEM to investigate the QCM becomes the trend of developing of products and save the cost of design and development. From previous studies [8-9] show there are many limitations in, such as, not easily implement and hard to construct the 3D model for general user to substitute real experiments. Recently, the computer-aids-design provides a power simulator for MEMS [10-11] design which able to work on the coupled field analysis, e.g. electro-mechanic, thermo-fluid by using finite element methods. An engineer can give accurate predication about the system without no prototype has been produced. The purpose of this article is to establish an efficient method of designing QCN by using commercial numerical package. The effects of QCN's resonant frequency influenced by the variation of the thickness of electrode and deposited mass are studied and compared with theoretical values and experimental data.

2. Transformation Matrix of AT-cut Quartz

Quartz is an oxide (SiO_2) and its material coefficient changes with cutting plane from different angles or directions. Therefore, with cutting from different angles or directions, quartz will have different resonant frequency and vibration modes. In the design of different devices, a particular cut of the crystal and wave propagation direction are chosen for high electromechanical coupling coefficient, temperature stability, and low losses.

AT-cut quartz crystal is the quartz crystal that cutting from a specific rotation around the X-axis $35^{o}15'$ and the TSM shown in Fig. 1. It is suitable for the substrate of quartz crystal nanobalance (QCN) due to its low temperature coefficient at room temperature than other kinds of quartz crystals as Fig. 2. Numerical procedures used in determining the properties of the crystal cut require the formulation of physical laws under coordinate transformation conditions. A very efficient transformation matrix has been developed for consideration of the coordinate system transformations in space of a rotation was proposed by [12-13]. Basically, it involves construction of 6 x 6 matrices that may be used to transform stress and strain by means of a single matrix multiplication. Using the derived transformation laws for the piezoelectric tensor for AT-cut and its transformation into the new system of coordinates obtained the equations as follow:

$$[C'] = [M][C][N]^{-1};\ [e']=[a][e][N]^{-1}$$
$$[d'] = [a][d][N]^{-1};\ [\bullet'] = [a]\,[\bullet][a'], \qquad (1)$$

where the Bond stress transformation matrix are **[M], [N]** and **[C]** elasticity matrix are 6 x 6 matrices, and piezoelectric stress **[e]** is a 3 x 6 matrix, **[d]** is the 3 x 6 piezoelectric strain matrix, **[ε]** is the dielectric matrix (evaluated at constant mechanical strain), and **[a]** is the coordinate transformation matrix (See Appendix I. for detail).

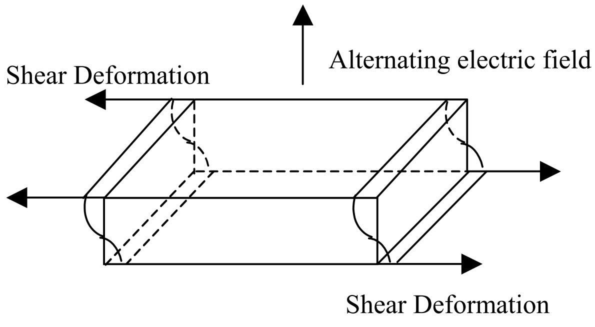

Fig. 1 *TSM vibration of AT-cut PQC*

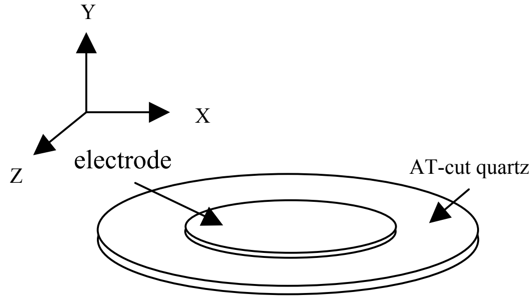

Fig. 2 *Geometrical model of QCN*

3. Quartz Crystal Nanobalance (QCN)

If applying an alternating electric field perpendicular to the surface of AT-cut quartz crystal, it will result in shear deformation of AT-cut quartz crystal and is called as thickness shear mode. If a small mass is deposited on the surface of AT-cut quartz crystal in air, it will result in decreasing the initial resonant frequency of AT-cut quartz crystal. It is a very special characteristic of mechanical vibration of QCN. The resulting frequency shift •F_q is proportional to the deposited mass Δm. Sauerbrey [1] derived the following equation to describe the relationship between •F_q and Δm:

$$\Delta F_q = -2.3 \times 10^6 \times F_q^{\,2} \times \frac{\Delta m}{A} \quad , \qquad (2)$$

where A is the area of electrodes and F_q is the resonant frequency of TSM. It is related to its thickness h_s, shows as

$$F_q = \frac{1}{2h_s}\left(\mu_q / \rho_q\right)^{1/2} \quad , \qquad (3)$$

where μ_q and ρ_q are the shear modulus and the density of quartz, respectively. The relationship between •F_q and Δm is also called "mass loading effect". It is the basic theory for the detection of analyzes in air of QCN.

4. Simulations and Discussions

In this section, The finite element numerical package ANSYS is applied to study effects of QCN's resonant frequency influenced by the variation of the thickness of electrode and deposited mass

[11,14]. The program provides a efficient tool for electromechanical coupled-field analysis and easily implemented for engineers. All simulate results are compared with the theoretical values.

4.1 Circular AT-cut PQC: Modal and harmonic analysis

Here, a circular PQC; without electrodes, represented as 3D-solid FE model is used to verify the accuracy of the finite element model. In the decision of element type, the coupled-field element solid 96 is chosen to simulate the AT-cut quartz. The anisotropic material properties of AT-cut quartz are given by Append II. which obtained from Eq. (1) respectively and the dimension of FE model is given in Table 1.

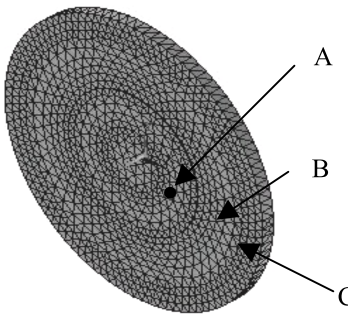

Fig. 3. *QCN FE model*

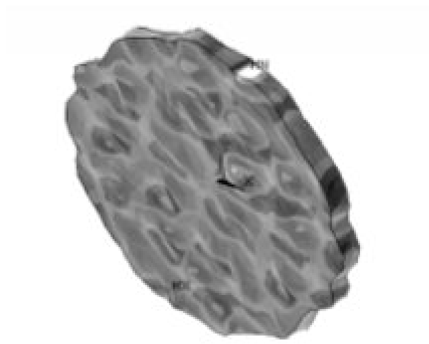

Fig 4. *TSM of 1.87MH AT-cut PQC*

Table 1. *Dimension of QCN*

(m)	1.87 MHz	9.5 MHz	10 MHz	50MHz
radius	0.006	0.006	.006	0.006
Thickness	0.883×10^{-3}	1.737×10^{-4}	1.3×10^{-4}	3.3×10^{-5}
Radius of electrodes	-	-	0.004	0.004
Thickness of electrodes	-	-	1×10^{-5}	2×10^{-7}

Table 2. *1.87MHz PQC resonant frequency comparison*

(MHz)	Theoretic value	Experimental value [8]	Simulated value
	1.87	1.89	1.87063
Error		1.07	0.034

The geometrical FE model of circular PQC used for modal and harmonic analysis were shown in Fig. 3 (A:mass,B:electrodes,C:quartz). Fig. 4 shows the plot of TSM mode shape of 1.87MHz PQC and

Table 2 indicates the simulated result of TSM resonant frequency analysis compared to the theoretic value and experimental result from [14]. Recently, the nanotechnology successfully develops a high frequency PQC to increase the sensitivity and accuracy. The Table 3 indicates the data of the comparisons of resonant frequency between the theoretic and simulated results. Next, a common used 9.5 MHz PQC is used for harmonic analysis and the corresponding spectrum is shown in Fig. 5 from the FEA. The results from the simulations indicate the FE model is corrected and good for further studies.

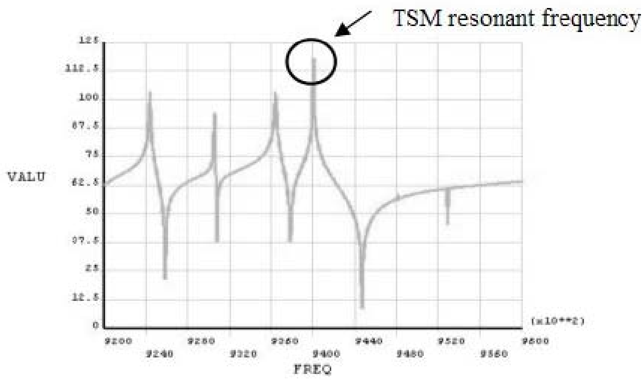

Fig. 5. *Corresponding spectrum of the 9.5 MHz AT-cut PQC*

4.2. The relation between the electrodes thickness and resonant frequency shift

The purpose of this section is to research the effect of QCN's resonant frequency influenced by the thickness of electrodes. Here, five different thickness of gold electrode are chosen to apply on the surface of a 10 MHz QCN and simulate the variation of QCN's resonant frequency. Table 3 shows the comparison of the simulate results and theoretical values. The initial frequency is the resonant frequency of bare AT-cut quartz, and the theoretical values are calculated by Eq. (3). Obviously, the simulated results agree well with the theoretical values, and the errors between these two values are less than 3%. Moreover, it indicates that the higher thickness of electrodes, the more QCN's resonant frequency decreases. The QCN's resonant frequency is proportional to its thickness of electrode.

Table 3.*The comparisons of different thickness of electrodes related to resonant frequency*

Electrode thickness (m)	Resonant frequency (Hz)	Initial frequency (Hz)	Simulate frequency shift(Hz)	Simulate frequency shift (Hz)	Theoretical frequency shift (Hz)	Error (%)
2×10^{-7}	9842745.56	10012464.57	169719.01	169719.01	170200	0.283
8×10^{-7}	9335561.46	10012464.57	676903.11	676903.11	680800	0.572
1×10^{-6}	9151677.55	10012464.57	860787.02	860787.02	851000	1.15

4.3 The simulation of QCN as gas sensor

In this section is to study the QCN is applied as a chemical gas sensor and the effect of resonant frequency influenced by the deposited mass is investigated. A common used 12 MHz PQC, thickness 1.3×10^{-4} m, is selected as the QCN quartz crystal. A 3D mass element is used to simulate the deposited mass. The simulated results show that the deposited mass is proportional to QCN's resonant frequency shift, i.e. the more deposited mass increase, the more QCN's resonant frequency shift increase. These results are the same as true physical phenomenon. Table 4 shows the simulated results of this case. The theoretical values of resonant frequency shift are calculated by Eq. (2), and the experimental data are obtained from [3]. Error A is the error between the simulation and theoretical values, and error B is the error between experimental and theoretical values. Obviously, the simulate results are more close to the theoretical values than experimental data.

Table 4 *Comparisons of deposited mass and resonant frequency shift*

CO_2Gas volume(L)	Mass (g)	Resonant frequency (Hz)	Initial frequency (Hz)	Simulated frequency shift (Hz)	Theoretical frequency shift (Hz)	Experimental frequency shift (Hz)[3]	Error(%)
2×10^{-9}	3.5728×10^{-9}	12760494.80	12760497.46	2.661	2.663	2.712	A:0.069 B:1.840
6×10^{-9}	1.0718×10^{-8}	12760489.36	12760497.46	8.100	7.989	8.223	A:1.392 B:2.929
1×10^{-8}	1.7864×10^{-8}	12760484.31	12760497.46	13.154	13.316	13.102	A:1.217 B:1.607

5. Conclusions

The purpose of this article is to establish a novel design tool for QCN by applying CAD/CAE numerical package and some conclusions shown as follow:

(1) It is the first experience of using finite element package works on QCN study. The results show not only generation of the structure model of QCN with ease but also simulation of QCN mass loading with accuracy.

(2) With many advantages, such as convenience, rapidity, accuracy, low cost, easy to implement and to learn. FEA simulator provides a new good couple-field design tool like, piezoelectric, electro-mechanical, thermo-fluid. It is useful for biosensor and micro-actuator in MEMS study in future.

(3) The resonant frequency shift is proportional to thickness of electrode and deposited mass and this phenomenon is called mass loading effect and the same as real physical behavior of QCN. Nevertheless, the comparison of simulate, theoretical and experimental data shows that the simulate results are more close to theoretical values than experimental data.

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Appendices

I. The operative matrices

$$[M]=\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \cos^2\xi & \sin^2\xi & \sin 2\xi & 0 & 0 \\ 0 & \sin^2\xi & \cos^2\xi & -\sin 2\xi & 0 & 0 \\ 0 & -\sin 2\xi/2 & \sin 2\xi/2 & \cos 2\xi & 0 & 0 \\ 0 & 0 & 0 & 0 & \cos\xi & -\sin\xi \\ 0 & 0 & 0 & 0 & \sin\xi & \cos\xi \end{bmatrix}$$

$$[N]=\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \cos^2\xi & \sin^2\xi & \sin 2\xi/2 & 0 & 0 \\ 0 & \sin^2\xi & \cos^2\xi & -\sin 2\xi/2 & 0 & 0 \\ 0 & -\sin 2\xi & \sin 2\xi & \cos 2\xi & 0 & 0 \\ 0 & 0 & 0 & 0 & \cos\xi & -\sin\xi \\ 0 & 0 & 0 & 0 & \sin\xi & \cos\xi \end{bmatrix}$$

$$[C]=\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ & C_{22} & C_{13} & -C_{14} & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & \text{symmetric} & & & C_{44} & C_{14} \\ & & & & & C_{66} \end{bmatrix} \quad C_{66}=(C_{11}-C_{12})/2$$

$$[a]=\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\xi & \sin\xi \\ 0 & -\sin\xi & \cos\xi \end{bmatrix}$$

$$[\varepsilon]=\begin{bmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{bmatrix}$$

$$[d]=\begin{bmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$[e]=\begin{bmatrix} e_{11} & -e_{11} & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -e_{14} & -e_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

II. Material property of AT-cut quartz

Stiffness (10^9 N/m^2)											
C_{11}	C_{12}	C_{13}	C_{14}	C_{22}	C_{23}	C_{24}	C_{33}	C_{34}	C_{55}	C_{56}	C_{66}
86.74	-8.25	27.15	-3.66	129.77	-7.42	5.7	102.83	9.92	68.81	2.54	29.01

Piezoelectric Strain (10^{-12}C/N)							
d_{11}	d_{12}	d_{13}	d_{14}	d_{25}	d_{26}	d_{35}	d_{36}
-2.3	1.2181	1.0819	-2.3917	-1.7213	3.3835	1.2165	-2.3913
Piezoelectric stress (C/m^2)							
e_{11}	e_{12}	e_{13}	e_{14}	e_{25}	e_{26}	e_{35}	e_{35}
0.171	-0.1551	-0.0159	0.0660	0.1097	-0.0935	-0.0775	0.0661

Permittivity (10^{-11} F/m)		
ε_{11}	ε_{22}	ε_{33}
3.9843	4.0138	4.0433
Density (kg/m^3) 2648		