

# Mass determination with piezoelectric quartz crystal resonators

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Early investigations on quartz crystal resonators indicated, that for small mass change, the frequency shift is linearly proportional to the added mass. The accuracy of mass determination was later improved somewhat by using the so-called "period measurement" technique, which assumes a linear relationship between added mass and change in period of oscillation. However, recent studies indicate that for large mass load, the elastic properties of the deposited material have to be taken into consideration. Based on the theory of one-dimensional acoustic composite resonators, an equation relating the resonant frequency of the composite system to the mass and acoustic impedance of deposited material can be derived. The equation shows that materials with different acoustic impedances will obey different mass-frequency relations. The experimental data for a number of materials with different elastic properties are shown to be in excellent agreement with the theoretical predictions to a mass load as large as  $50 \times 10^{-3}$  g/cm<sup>2</sup>. The results indicate that if the acoustic impedance of the deposited material is known, quartz crystal resonators can be used for measuring a large deposited mass to a remarkable accuracy by using the proper formula.

## INTRODUCTION

The possibility of using piezoelectric quartz resonators as mass sensing devices was first explored by Sauerbrey in 1957.<sup>1,2</sup> It was found that for a small mass uniformly deposited over the crystal surface, the shift in resonant frequency is linearly proportional to the mass. Furthermore, with the simple theory postulated, the frequency shift was found to be independent of the physical properties of deposited material. This means that the deposited mass can be determined by simple frequency measurements without the knowledge of its physical properties. Because of this simplicity, piezoelectric quartz crystal microbalances have been extensively used in thin film deposition processes as thickness and rate monitors. The accuracy of mass determination by those instruments was adequate for most applications provided that the restriction on small mass load could be observed. Typically, for a 5-MHz AT-cut quartz crystal, the error is less than 2% for a total mass load of less than  $2 \times 10^{-3}$  g/cm<sup>2</sup>.

Recently, attempts have been made both to extend the mass loading capability of quartz crystals and to improve the accuracy of mass determination. A different formula relating the deposited mass to the resonant frequency of quartz crystal has been employed in a number of commercial instruments since 1969. The measuring formula assumes a linear relationship between the change in period of oscillation and the deposited mass. This became the so-called "period measurement" technique. However, the elastic properties of

deposited material do not enter into the mass-frequency formula either. Early experimental results indicated that the adoption of this modified formula could indeed provide a significant improvement in accuracy of mass determination, especially for quartz crystals with large mass load.<sup>3,4</sup>

A recent study made by Lu and Lewis<sup>5</sup> on quartz crystal resonators indicated that for precise mass determinations, the elastic properties of deposited material have to be taken into consideration. Based on the analysis of one-dimensional composite acoustic resonators,<sup>6</sup> an equation can be derived which relates the resonant frequency of the composite system not only to the mass of deposited material, but also to its acoustic impedance. This theoretical equation has been shown to be in good agreement with experimental results. Since the results represent a significant departure from previous studies on quartz crystal microbalances, it was decided that a more extensive experimental study should be made to test the range of validity of the theoretically derived equation. In the present study, quartz crystals with resonant frequencies ranging from 4 to 6 MHz were investigated. The mass load on these crystals was extended to as large as  $50 \times 10^{-3}$  g/cm<sup>2</sup>.

## THEORETICAL BACKGROUND

The resonant frequency  $f_q$  of a quartz crystal plate oscillating in the fundamental thickness shear mode is determined by its thickness  $t_q$  according to the equation

$$f_q t_q = v_q / 2, \quad (1)$$

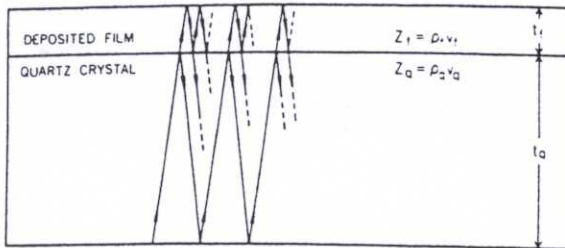


FIG. 1. Schematic representation of a one-dimensional composite resonator consisting of a quartz crystal and a deposited film. The direction of acoustic wave propagation is actually perpendicular to the surfaces of the resonator.

where  $v_q$  is the shear wave velocity along the direction of thickness. For AT-cut quartz crystal,  $v_q$  equals to  $3.336 \times 10^5$  cm/sec.

From Eq. (1), the resonant frequency shift  $df_q$  caused by an infinitesimal change in crystal thickness  $dt_q$  should obey the relation

$$df_q/f_q = -dt_q/t_q. \quad (2)$$

Equation (2) can also be written in terms of crystal mass  $m_q$  and change of crystal mass  $dm_q$ . One thus has

$$df_q/f_q = -dm_q/m_q. \quad (3)$$

In order to justify the use of Eq. (3) for mass determination, Sauerbrey postulated that for small mass change, the addition of foreign mass can be treated as a mass change of quartz crystal.<sup>2</sup> Equation (3) thus becomes

$$df_q/f_q = -dm/m_q, \quad (4)$$

where  $dm$  is an infinitesimal amount of foreign mass uniformly distributed over the crystal surface. If one assumes the validity of Eq. (4) for an arbitrary but small mass change, it can be written in the form of

$$m_f = m_q(f_c - f_q)/f_q \quad (5)$$

for determining the mass of thin film  $m_f$ , where  $f_c$  is the resonant frequency of quartz crystal with the deposited film. If the film density  $\rho_f$  is known, the film thickness  $t_f$  can be calculated by using the following equation:

$$\rho_f t_f = (\rho_q t_q / f_q) (f_c - f_q), \quad (6)$$

where  $\rho_q$  is the density of quartz.

Equation (6) predicts that the frequency shift is linearly proportional to the deposited mass and not affected by the physical properties of the film. Although Eq. (6) is supported by early experimental data, the substitution of quartz with a mass equivalent of foreign material needs theoretical justifications. Stockbridge<sup>7</sup> thus applied a Rayleigh perturbation analysis to the problem and obtained a mass-frequency relation same as Eq. (6). The basic assumption is that there is no potential energy stored in the added mass during oscillation. This assumption can perhaps be justified for very thin films if one considers the discontinuous nature of film structure and the surface roughness of the quartz crystal. However, as the mass of deposited material

becomes appreciable and forms a uniform layer of finite thickness, the assumption that acoustic waves do not propagate in the film becomes less acceptable.

In an effort to rectify the difficulties, Miller and Bolef<sup>8</sup> took a different approach and treated the quartz-film combination as a composite acoustic resonator. The system, shown in Fig. 1, consists of a film characterized by thickness  $t_f$ , shear wave velocity  $v_f$ , and density  $\rho_f$ ; and a quartz crystal characterized by corresponding parameters  $t_q$ ,  $v_q$ , and  $\rho_q$ . The quantities  $Z_f = \rho_f v_f$ , and  $Z_q = \rho_q v_q$  are known as the shear-mode acoustic impedance of film and of quartz crystal respectively. If the film is separated from the quartz crystal, a mechanical resonant frequency obeying the relation

$$f_f = v_f / 2t_f \quad (7)$$

can be defined for the film while the resonant frequency of quartz crystal obeys Eq. (1). Because  $Z_f$  is generally different from  $Z_q$ , a continuous acoustic wave propagating in the direction perpendicular to the surface will be partially transmitted and partially reflected at the film-quartz interface. The result is the formation of a complicated multiple interference pattern which determines a set of resonant frequencies of the composite system. If one assumes total reflection of waves at both surfaces and neglects the acoustic losses in both mediums, the resonant frequency of composite system  $f_c$  can be determined by the following equation [Eq. (9) of Ref. 6]:

$$2r[\cos(2\pi f_c/f_f) - \cos(2\pi f_c/f_q)] + (1+r^2)[1 - \cos(2\pi f_c/f_q) \cos(2\pi f_c/f_f)] + (1-r^2) \sin(2\pi f_c/f_q) \sin(2\pi f_c/f_f) = 0, \quad (8)$$

where  $r = (Z_q - Z_f)/(Z_q + Z_f)$  is the reflection coefficient. By retaining only terms to second order in the series expansion of the trigonometric functions, it can be shown that for small added mass, Eq. (8) reduces to the original Sauerbrey's result. Miller and Bolef's approach was certainly more realistic for cases involving uniformly deposited films of well defined thickness, while Stockbridge's theoretical argument appeared to be appropriate for extremely thin films. Fortunately, both approaches yielded the same result. Therefore, the application of Eq. (5) for determining small deposited mass can be theoretically justified.

The utilization of Eq. (5) for mass determination began to encounter difficulties when attempts were made to extend the mass loading capability of quartz crystals. While improvements made in the crystal design and mounting technique enabled the quartz crystal to remain oscillating for large mass load, the error in mass determination became less tolerable. More seriously, when the quartz crystal microbalance is used to measure the rate of mass change, such as thin film deposition rate, the error is even greater. This is because the error in mass measurement itself becomes a time varying function and increases with respect to time.

A commonly used method for improving the accuracy of quartz crystal microbalance with large mass load is the so-called "period measurement" technique.<sup>3,4</sup> This technique involves the use of the following equation for mass determination:

$$\rho_t t_t = \rho_q t_q f_q (1/f_c - 1/f_q). \quad (9)$$

Since  $1/f_c$  and  $1/f_q$  are the periods of oscillation for the quartz crystal resonator with and without the deposited film, Eq. (9) implies that the deposited mass is linearly proportional to the change in period of oscillation. Equation (9) can be obtained by differentiating Eq. (1) and writing it in the form of

$$d(1/f_q) = (2/v_q) dt_q. \quad (10)$$

The deposited mass is then treated as a mass equivalent of quartz, or, in other words,  $dt_q$  is replaced by  $(\rho_t/\rho_q) dt_t$ . An integration of

$$d(1/f_q) = (2/v_q) (\rho_t/\rho_q) dt_t \quad (11)$$

thus yields Eq. (9). However, since the treatment of deposited mass as a mass equivalent of quartz has already been challenged even for small mass loads on quartz crystals, it is difficult to accept the same argument, in the derivation of Eq. (9), for large mass loads. Even though the improvement in accuracy of mass determination by using Eq. (9) has been supported by experimental evidence, it can nevertheless be considered as an empirical equation only.

A different approach to improve the accuracy of quartz crystal microbalance was suggested by Lu and Lewis.<sup>5</sup> Equation (8) clearly indicates that the resonant frequency of a composite system is also determined by the acoustic properties of the deposited film. Therefore, its effect on the accuracy of mass determination by a quartz crystal resonator was reexamined. It was found that the complicated expression of Eq. (8) can be reduced to a much simpler form of

$$\tan(\pi f_c/f_q) = -(1/Z) \tan(\pi f_c/f_t), \quad (12)$$

where

$$Z = Z_q/Z_t = \rho_q v_q / \rho_t v_t \quad (13)$$

is the shear-mode acoustic impedance ratio between the quartz crystal and deposited film. For mass determination purposes, Eq. (12) can be expressed in the form of

$$\rho_t t_t = [\rho_q t_q f_q / \pi Z f_c] \tan^{-1} \{ Z \tan[\pi(f_q - f_c)/f_q] \}. \quad (14)$$

If one introduces two dimensionless parameters,

$$M = \rho_t t_t / \rho_q t_q \quad (15)$$

and

$$F = (f_q - f_c) / f_q, \quad (16)$$

as the reduced areal density and reduced frequency shift, respectively, Eq. (14) becomes

$$M = \{1/[\pi Z(1-F)]\} \tan^{-1}(Z \tan \pi F). \quad (17)$$

Figure 2 is a plot of Eq. (17) with different values of  $Z$ . It shows that deposited materials with different acoustic impedances will follow different mass-frequency rela-

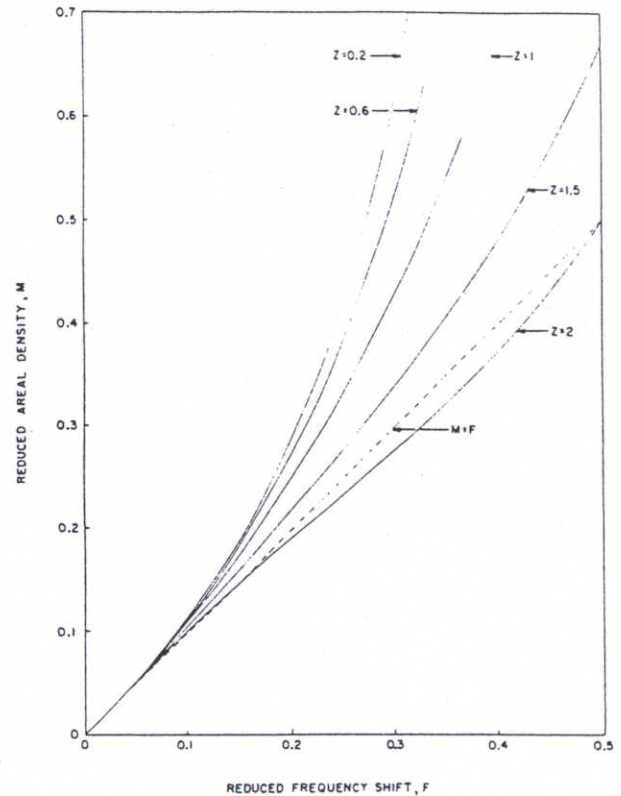


FIG. 2. Reduced areal density  $M$  as a function of reduced frequency shift  $F$  for different values of shear-mode acoustic impedance ratio  $Z$ . The dashed line representing  $M = F$  is included for comparison purpose.

tions. The differences become increasingly large as the mass load on the quartz crystal increases. This prediction has been confirmed by experimental results.

It can easily be verified that Eq. (9) is a special case of Eq. (14) with  $Z=1$ , or for the case of a perfect acoustic impedance match (quartz on quartz). For small frequency shift, that is,  $f_c \approx f_q$ , Eq. (14) reduces to Eq. (6). Equation (6), which is equivalent to

$$F = M, \quad (18)$$

is also shown in Fig. 2 for comparison purposes. One can see in the figure that Eq. (18) represents a closer approximation of Eq. (14) with  $Z=2$  than Eq. (9) does. In practice, however, materials commonly used in thin film deposition processes have  $Z$  either close to or less than unity. This explains the improvement in accuracy of mass determination resulting from the so-called "period measurement" technique Eq. (9) with  $Z=1$ , but also shows that such improvement is rather coincidental.

## EXPERIMENTAL TECHNIQUE

The quartz crystals used were AT-cut with fundamental series resonant frequencies ranging from 4 to 6 MHz. The crystals were 1.40 cm in diameter with beveled edges and slight convex contouring of one or both surfaces. Each crystal was coated with circular

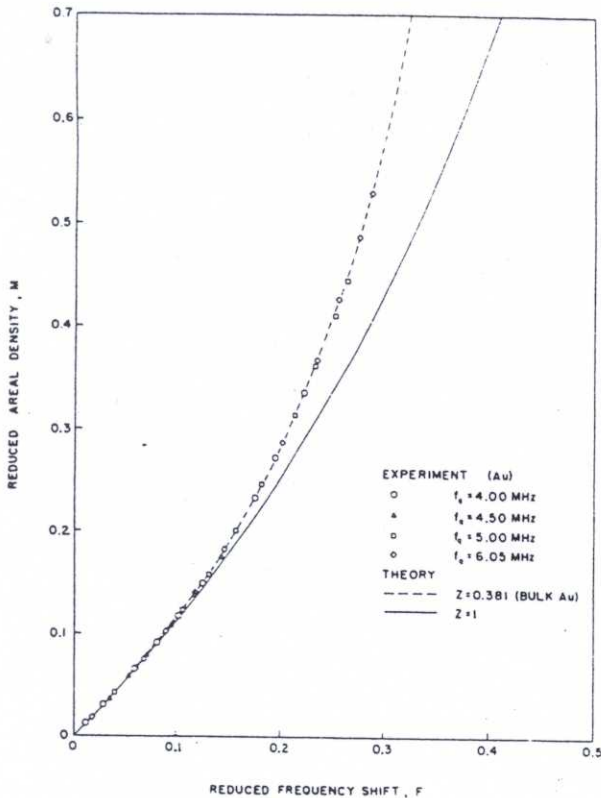


FIG. 3. Comparison between experimental data for gold on crystals with different resonant frequencies and Eq. (17) with  $Z = 0.381$ . The curve representing Eq. (17) with  $Z = 1$  ("period measurement" technique) is also shown for comparison purpose.

aluminum electrodes on both sides. The electrodes were several hundreds angstroms thick and 1.30 cm in diameter. High-purity materials were evaporated from an electron beam source in a conventional vacuum system. No attempts were made to keep the deposition rate constant. The crystals were exposed to evaporant on one side through masks with a circular opening of the same diameter as the electrodes. After each deposition, the mass on individual crystals was measured to a precision of  $\pm 1 \times 10^{-6}$  g by a Sartorius 2405 microbalance. The areal density was then calculated from the deposited mass dividing by the area of deposition. This is the same quantity as  $\rho t$ . Therefore, it was not necessary to know the density and thickness of the film separately.

For the measurement of resonant frequency, the crystal was placed in a crystal holder and held by finger springs near the edge to minimize the effect of acoustic coupling. The crystal was connected to an oscillator circuit and its output was measured by a digital frequency counter. With proper adjustment of the component values in the oscillator circuit, crystals with frequency shifts as much as 40% of their original frequencies could often be made to continue oscillating.

It was difficult to precisely determine the thickness of a quartz crystal because its surfaces were slightly contoured. The quartz crystal thickness  $t_q$  was therefore determined by using Eq. (1) with the known  $f_q$  rather

than by actual measurement. A density of  $2.648 \text{ g/cm}^3$  was used for quartz.<sup>9</sup>

Although  $f_q$  is defined as the resonant frequency of the quartz crystal with no deposited material (including the electrodes), using the resonant frequency of a crystal with the thin aluminum electrodes for  $f_q$  caused a difference of less than 0.1% in mass determinations. This was understandable because the electrodes were very thin and aluminum matches very well with quartz both in density and acoustic impedance. Thus, the resonant frequencies of crystals with the electrodes were treated as  $f_q$  in most of the computations.

## RESULTS AND DISCUSSION

The resonant frequency of a quartz crystal  $f_q$  does not show up in Eq. (17) because it is absorbed into the reduced parameters  $F$  and  $M$ . This means that for a specific material, mass-frequency relations of crystals with different resonant frequencies can be represented by a single curve of  $M$  vs  $F$ . This prediction was confirmed by experimental data obtained on all materials being studied. The results for gold deposited on crystals with different  $f_q$  are shown in Fig. 3. The value of  $Z$  for gold was obtained from its bulk properties.<sup>10</sup> The results indicate that the resonant frequency of the quartz crystal does not affect the accuracy of mass determination.

The range of validity of Eq. (17) was also experi-

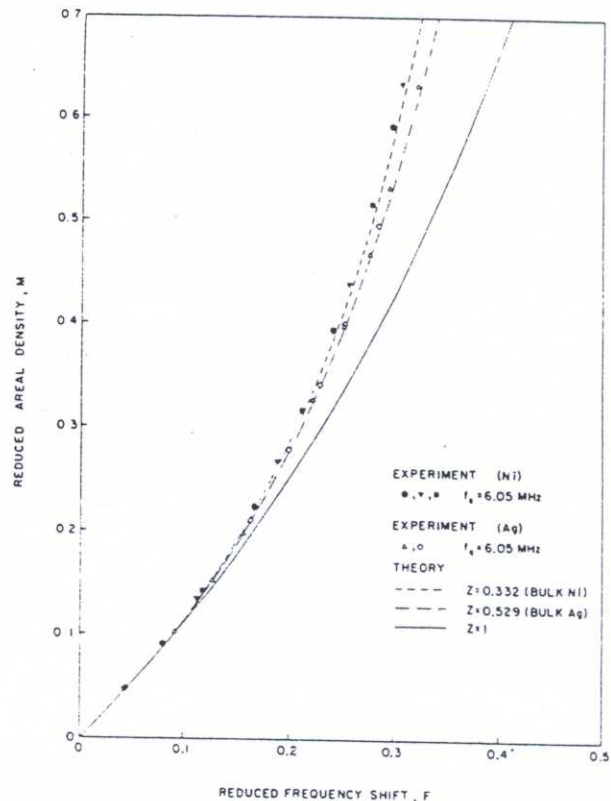


FIG. 4. Comparison between experimental data and Eq. (17) for nickel and silver.

mentally tested using materials of different  $Z$  and very large mass loads. Figure 4 shows experimental results for nickel and silver. The data for aluminum and copper are shown in Fig. 5. Again, all values for  $Z$  were calculated from properties of bulk materials.<sup>10</sup> It should be noted that some of the experimental data points represent a mass load of close to  $50 \times 10^{-3} \text{ g/cm}^2$  on the quartz crystal. For aluminum on 6-MHz crystals, the thickness of such deposited mass equals to about 70% of the quartz crystal. Considering the possible differences in acoustic properties between film and bulk materials, the agreement between experimental data and theoretical equations using the bulk properties is remarkably good.

There are several factors which can affect the accuracy of Eq. (17) for mass determination. The most significant factor appears to be the stress in the films. With a very thick film on the crystal, the crystal surface distortion due to stress could easily be observed. For all materials examined in this study, the surface with the deposited film always became concave. This is consistent with the fact that for normal deposition temperatures, the stress in metal films is typically tensile, i.e., the film contracts in the plane of the surface. The existence of tensile stress in the film can cause the resonant frequency of an AT-cut quartz crystal to be higher than that in a stress free state.<sup>11</sup> This means that the observed values for  $f_c$  are higher than normal. Consequently, the calculated values for  $(f_q - f_c)/f_q$  are less than the actual values. This will cause a shift of experimental points to the left of the curves representing the theoretical equations.

The magnitude of this deviation can be quantitatively correlated to the estimated magnitude of stress in the quartz crystal. The presence of large stress in deposited copper and nickel films is well known. Silver and gold are known as materials producing films with relatively low stress. It should also be realized that for a specific areal density, the film thickness is inversely proportional to its density. Therefore, if the stresses produced in gold and aluminum films are of the same magnitude, the stress in the quartz crystal caused by an aluminum film will be almost one order of magnitude higher than that caused by a gold film of equal areal density.

The propagation of acoustic waves in the deposited film is also affected by the presence of static stress. Additionally, it is reasonable to assume that the acoustic impedance of deposited films should be slightly different from that of bulk materials due to structural and density differences. These can also be the contributing factors to the observed differences between experimental data and theoretical equations using bulk properties.

For materials examined in this study, the error in mass determination between experimental data and theoretical predictions using acoustic impedance for bulk material is less than 3% even for the worst case. If measurements of higher precision are required, one can use an empirically determined value of  $Z$  in Eq. (14) for mass determination. For example, in Fig. 5, the experimental points for aluminum can be brought to a

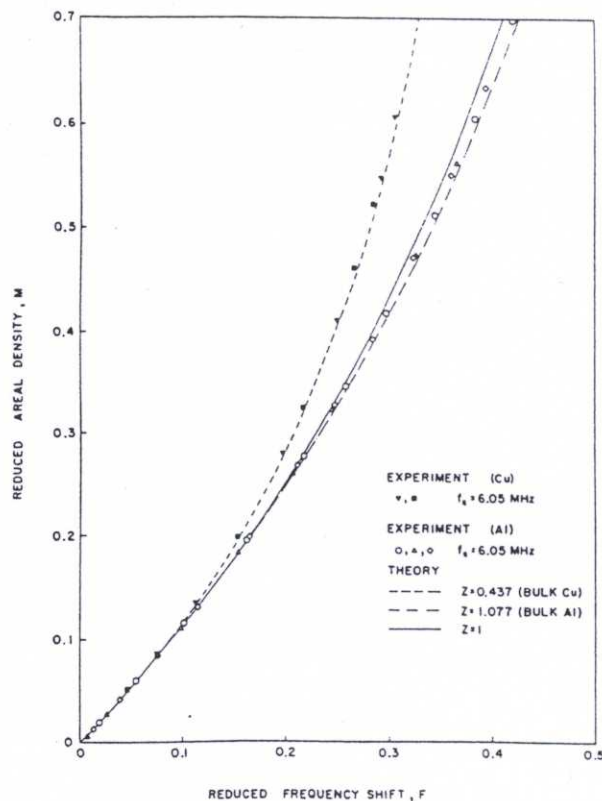


FIG. 5. Comparison between experimental data and Eq. (17) for copper and aluminum.

nearly perfect fit of a curve representing Eq. (17) with  $Z = 1.04$ .

## CONCLUSION

The present study examined the validity range of mass-frequency relations derived from an acoustic analysis of one-dimensional composite resonators. The results showed that Eq. (17) is valid for a mass load of at least  $50 \times 10^{-3} \text{ g/cm}^2$  and for materials of different acoustic impedances. It is also valid for crystals with resonant frequencies ranging from 4 to 6 MHz. The experimental data demonstrated, without ambiguity, that for precise mass determination by quartz crystal resonators, especially for crystals with large mass load, the elastic properties of the deposited film have to be considered. Good accuracy of mass determination can be obtained by using the acoustic impedance of bulk material for  $Z$  in Eq. (17). It is possible to further improve the accuracy by employing an experimentally determined value of  $Z$  for the deposited film.

Since Eq. (17) is relatively simple and contains only one more material constant other than the density of deposited film, namely, the acoustic impedance ratio  $Z$ , it can be programmed into an instrument using modern digital circuitry. Real-time measurements of thickness and rate during thin film deposition processes can thus be made. It appears that the outstanding problems of quartz crystal microbalances at the present time are

generally practical ones such as the activity and stability of the crystals.

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