Improvement in Q-factor of AT-cut Quartz Crystal Resonators using Single Walled Carbon Nanotubes

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***Abstract*— Use of higher operating frequencies and integration with VLSI circuits and MEMS are driving the need for smaller and thinner quartz crystal resonators (QCRs). Implicit in such scaling is the maintenance of *Q*-factor of the resonator necessary for achieving the required frequency stability. The intrinsic *Q*-factor of the resonator is inversely proportional to the resonance frequency, limiting the maximum *Q* that can be achieved. Recent research in this field has been directed towards increasing the *Q*-factor of these resonators, including reduction of surface roughness, decreasing support losses by reduction of resonator thickness, making resonator surface convex to increase energy trapping, etc. In this paper we report the first observation of the increase in the quality factor of an *AT*-cut quartz resonator through deposition of thin layers of single walled carbon nanotubes on its electrodes.**

Keywords - quartz, resonators, bulk acoustic wave (BAW), single wall carbon nanotubes (SWNTs), Q factor, miniaturization, micromachining.

I. INTRODUCTION

Miniaturized quartz resonators are currently used as standard frequency references in mobile phones, computers, etc. The continually shrinking size of these electronic devices is driving the need for even smaller quartz resonators. Further, the progressively higher operating frequencies being used in these electronic devices is another reason fueling the need for thinner crystal resonators, since the resonance frequency of a bulk acoustic resonator is inversely proportional to the thickness of the resonator. However, to obtain high quality (*Q*-) factor in resonators, it is necessary that an optimal thickness to lateral size ratio of the resonator be maintained enabling higher drive efficiency and effective energy trapping necessary for achieving high *Q*-factors. Maintaining high *Q*-factors in miniaturized quartz resonators is necessary since it determines the frequency stability of the resonator. The higher the *Q* factor, the lower is the noise floor and hence more stable is the resonance [1]. There have been several attempts to increase the quality factor of the resonators, including reduction of surface roughness [2], reduction of support losses by reduction of resonator thickness [3], making resonator surface convex to increase energy trapping [4], etc. In this paper, we present the use of an overlayer of Single Walled Carbon Nanotubes (SWNTs) to increase the *Q*-factor of resonators.

Since their discovery by Iijima *et. al.* in 1991, carbon nanotubes have been found to have unique physical, chemical and electronic properties [5]. They are one of the stiffest material known [6], excellent field emitters due to high electric fields generated at the end caps [7], and natural reservoirs of gases [8]. In addition to advancements in understanding the properties of carbon nanotubes, there have been significant advancements in quartz micromachining technology. It is now possible to realize very small and thin quartz resonator substrates with excellent control over their surface roughness and dimensions. Control over the surface roughness can be achieved by the use of Inductively Coupled Plasma (ICP) based dry anisotropic reactive ion etching (RIE) processes. Using SF_6/Ar based chemistry, we have been able to achieve rms surface roughness as small as 1.97 nm at relatively high etch rates of ~0.5 μm/min [9]. Traditionally, wet etching techniques based on HF chemistry have been used for micromachining of quartz resonators. However, these processes suffer from problems such as formation of several microtrenches on the surface at high etch rates (1 μm/min) and relatively smooth surface finish (~10 nm), and relatively low etch rates (0.25 μm /min) and high surface roughness (> 120 nm) when these microtrenches are avoided [10].

II. EXPERIMENTAL METHODS

Miniaturized AT-cut quartz resonators in an inverted mesa configuration were fabricated using an ICP-RIE process with electrode diameters ranging from 100μm – 1mm, and thickness ranging from 33μm (49 MHz) – 90μm (19 MHz). This resulted in quartz resonators with *Q*-factors ranging from ~500 to ~7500, depending on the individual geometry. As expected, the larger the ratio of diameter to thickness of the resonator, the higher was the obtained *Q*-factor. An rms surface roughness of less than 2 nm was obtained at 350 W of substrate power, 150 W of ICP power, 6 sccm of Ar, 3 sccm of SF_6 and a process pressure of less than 3 mTorr. The details of the etch process and the fabrication of the AT-cut resonator are given elsewhere [9]. A solution of *debundled* SWNTs (a mixture of ~1/3 metallic and ~2/3 semiconducting nanotubes procured from Carbolux Inc.) in NMP (N-methyl-2-pyrrolidinone) was prepared along the route described in detail recently [11]. The density of the solution was 10 mg/ml (mass of SWNT/volume of NMP). AFM measurements were made to determine the fraction (~80-90%) of tubes appearing as single isolated tubes on the substrate. The SWNTs were typically ~1.4 nm in diameter and ~800nm in length. The solution was then sprayed in controlled bursts over the QCM

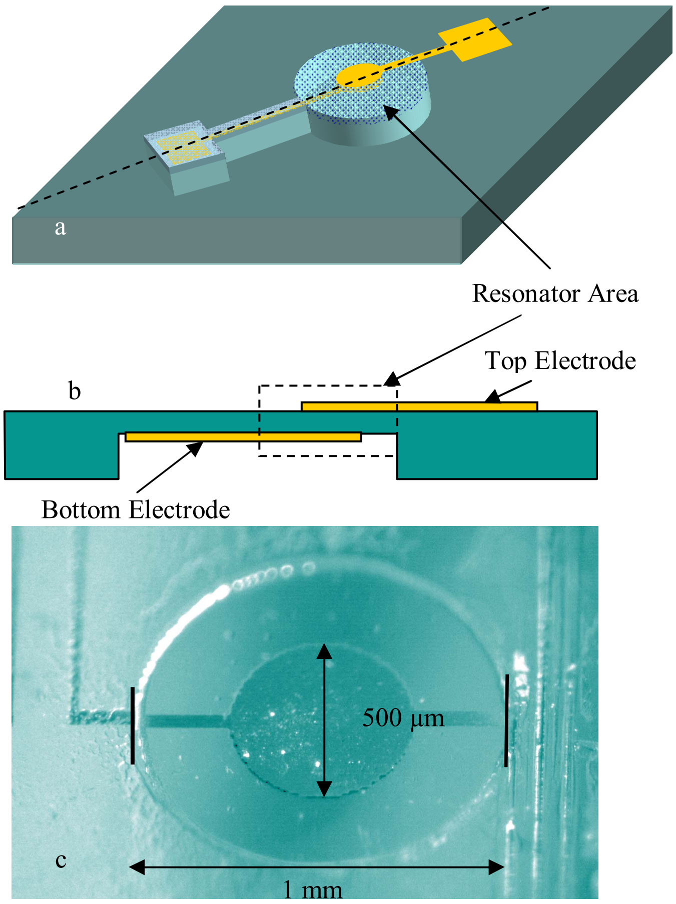

Figure 1: *(a) A 3D schematic diagram of the micromachined quartz resonator, (b) Cross-sectional view of the resonator along the dashed line shown in (a), and (c) Optical picture of the fabricated quartz crystal resonator showing the etch pit and the gold electrode (Note: The optical image shows the opposite face of the resonator in comparison to the schematic illustration to highlight the etched surface). The diameter of the etched diaphragm was 1 mm and the diameter of the Au/Cr (100nm/20nm) electrode was 500 µm. The diaphragm was etched in a 1" AT-cut quartz disc, 110µm thick, obtained from Boston Piezo-Optics Inc. The final thickness of the diaphragm realized was ~ 56 µm.*

surface using an air brush. The NMP solvent was allowed to evaporate, leaving behind a randomly oriented, uniform deposit of SWNTs on the gold electrode and the surrounding quartz surface of each resonator.

The resonator was connected to an Agilent 4294A impedance analyzer and the in-phase and quadrature impedance of the resonator around the resonance frequency were acquired in real-time using a Labview® based program. At resonance, the phase of the resonator was numerically fitted with a Lorentzian lineshape for an accurate determination of the center frequency and the *Q*-factor. The measurements were taken before and after coating the surface with the nanotubes, in laboratory atmosphere and in vacuum (~$6.5\text{x}10^{-4}$ mbar). These resonators were configured to operate as Quartz Crystal Microbalance (QCM) enabling readout of the mass of carbon nanotube deposited on the surface and also the amount of desorption of gases contained in the carbon nanotubes when the resonators were kept in vacuum. The change in the resonance frequency for a QCM with change in mass on its electrodes is given by the Sauerbrey equation as–

$$\Delta m\big/A = -\left(\sqrt{\rho_q\mu_q}\Big/2f_0^2(0)\right)\left(\frac{9.6\times10^{-8}\,f_0(0)}{Q}\right) \qquad (1)$$

where, μ_q and ρ_q are the shear modulus and the density of quartz respectively, and A is the area of the electrode on the quartz crystal [12]. From equation (1), the minimum achievable mass resolution depends on the maximum *Q*-factor achievable. The results and their analysis presented in this letter are for a representative sample having electrode diameter of 500 µm and thickness of ~56 µm.

TABLE I

Quality factors of three typical resonators. The Q factors increase when the resonators are coated with SWNTs. The Q factors increase further when the coated resonator is put into vacuum due to desorption of gases from carbon nanotubes resulting in reduction in the viscoelastic dissipation.

Q-Factor of as Fabricated Resonator	*Q*-Factor of Resonator Coated with SWNT in Air	*Q*-Factor of the Resonator Coated with SWNT in Vacuum
580	**989**	**1136.6**
949	**1588**	**1924**
6986.3	**8188.6**	**15141.8**

III. RESULTS AND DISCUSSION

As expected, upon sequential loading of the crystal with SWNTs, the resonance frequency of the crystal decreased according to the Sauerbrey equation with an average of 3.27 ng of SWNTs deposited on the resonator surface for each loading step (Fig 2). At the same time, the *Q*-factor of the resonators increases when increasing number of carbon nanotubes are added to the surface of the resonator, as shown in Fig 2. Similar results were obtained for all the studied resonators. Table I summarizes the results for three representative samples. Since SWNTs are known to be store house of gases [5], we suspected that these gases could cause viscoelastic dissipation in the resonating crystal. The typical desorption time constants of gases from SWNTs has been reported to be several days [8] even at high temperatures of 500 K. Hence the coated resonators were subjected to vacuum (~6.5e-4 mbar) over a period of 24 hours and 48 hours. It was observed that desorption over such time periods follow a characteristic logarithmic curve with respect to time, as shown in Figure 3. This indicates that the desorption process is probabilistic with desorption rate decreasing as the number of physisorbed and trapped gas molecules on SWNTs decreases with time in vacuum. Also, it was observed that the *Q*-factor of the resonator increased by as much as 15% when kept in vacuum over a period of 24 hours. This is because of reduction in viscoelastic dissipation due to reduced gas content of the carbon nanotubes on the surface of the resonator. As shown in Figure 2, this trend of an increase in *Q*-factor was consistent for all cases of SWNT loading. Another point worth noting is that the relative amount of change in the *Q*-factor when the resonators are kept in vacuum increases with increasing amount of carbon nanotubes on the surface of the resonator. This is because more the number of carbon nanotubes, the greater are the number of physisorbed, chemisorbed and trapped gas molecules in them and hence greater is their contribution to viscoelastic damping in the resonator. Consequently, greater is the percentage increase in the *Q*-factor due to increasing desorption of these gas molecules when the nanotube coated resonators are kept in vacuum.

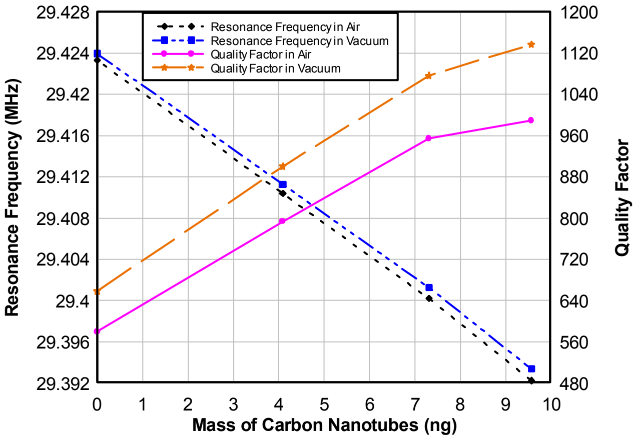

Figure 2: *The quality factor of the resonator increases with sequential loading of SWNTs. A direct evidence for the deposition of SWNTs is indicated from the decrease in the resonance frequency as more and more SWNTs are added on the surface. When the coated resonators are subject to vacuum (~6.5e-4 mbar), the Q-factor increases further due to desorption of physisorbed, chemisorbed, and trapped gas and solvent molecules in the SWNTs. Correspondingly, the resonance frequency increases in vacuum because of desorption of mass (gas and solvent) molecules from its surface.*

The change in the *Q*-factor can be related to the throughput of degassing from the SWNTs which is given by [13]

$$Q_{PV,\ degas} = \frac{a_1 A}{(t)^{\alpha}}, \tag{2}$$

where $Q_{PV,degas}$ is the rate of desorption from the SWNTs, a_1 is the degassing rate per unit area, A is the area of the surface over which SWNTs have been deposited, t is the time, and α is determined by the desorption throughput decay. From the experimental curve shown in Fig. 3, the value of α was obtained as 0.26, which as compared to 1 for mild steel, is very small. This implies that desorption process from SWNTs decays slowly as compared to steel surfaces. This is to be expected since the trapped gas molecules from within the nanotubes are expected to take a very long time to come away and this essentially translates into a very low desorption throughput decay.

As shown in Fig. 3, desorption process is observed to be reversible, wherein upon the release of vacuum and operation of the resonator in air, the gas molecules are readsorbed/trapped causing the resonator to revert back to near its original *Q*-factor before the application of vacuum. However, the recovery of the resonator *Q*-factor is not 100%. For the resonator shown here, the *Q*-factor of the crystal loaded with SWNTs increased from 914 in air to 1170 in vacuum after ~30 hrs. However, even a prolonged re-exposure to air ambient decreased the *Q*-factor to only 944. This is consistent with published reports that uptake of gas molecules for SWNTs is much slower than desorption in a vacuum ambient [8]. Additionally, contribution is also expected from the irreversible volatilization of NMP molecules from the surface of the resonator after vacuum desorption from SWNTs.

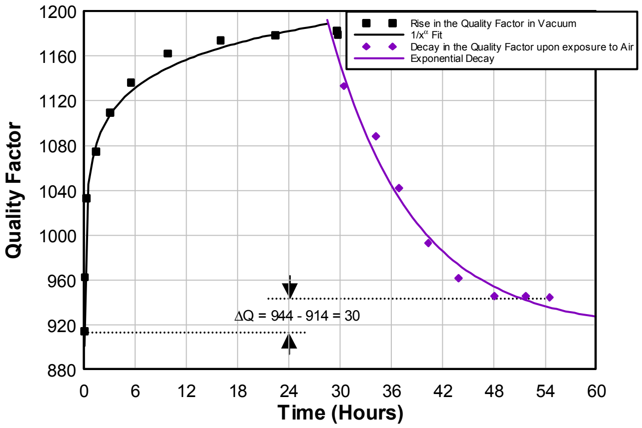

Figure 3: *The Q-factor of the resonator coated with SWNTs increases when kept in a vacuum of ~6.5E-4 mbar over several hours. The increase follows a characteristic $1/x^{\alpha}$ law indicating the desorption process of gases from the SWNTs on the surface of the resonator is probabilistic. When the vacuum is released and the resonator operated in air, some of the gases are readsorbed causing the resonator Q-factor to decrease.*

The resonance curves were fitted with the Butterworth Van Dyke (BVD) circuit model [14] and values of static capacitance (C_0), motional capacitance (C_m), motional resistance (R_m) and motional inductance (L_m) were extracted. A small change in the L_m value consistent with the sequential mass loading of the nanotubes was observed. The values of all the other parameters, except the motional resistance, remained constant during the sequential depositions of SWNTs. As shown in Figure 4, the R_m decreases substantially with sequential loading of SWNTs and upon subjecting the nanotube coated resonator to vacuum. The experimentally measured *Q*-factor showed a $1/R_m$ dependence (Fig. 4) and is consistent with the expression $Q = \omega * L_m / R_m$ [14], when as in this case the product of ω the parallel resonance frequency of the resonator and L_m shows little dependence upon the nanotube deposition.

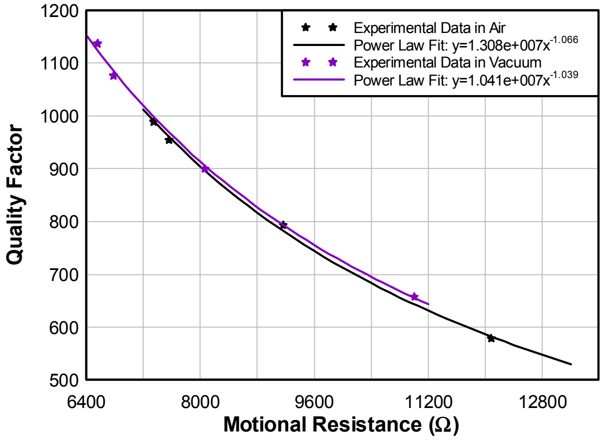

Figure 4: *Q-factor of the resonator as a function of the motional resistance of the resonator shows the expected 1/x dependence for both air and vacuum ambients as seen by the curve fits.*

Except for SWNTs, the use of other conventional over layers and thin films always caused a decrease in the *Q*-factor of the resonator. We present two plausible explanations for the observed behavior. It has been shown that there is coupling between bulk acoustic waves (BAW) and surface acoustic waves (SAW) in SAW resonators due to the presence of random surface roughness [15]. We assume that this should be true for BAW devices also, causing generation of surface acoustic waves in our thickness shear mode resonator. Unlike the BAW which are essentially confined due to energy trapping, the SAW are unconfined, and will propagate away along the surface of the quartz crystal dissipating their energy. Even though the SWNT film is held on the surface by the van der Waals force, our data is consistent with the view that the film acts to stiffen the surface and suppresses the coupling of energy into surface acoustic modes. Further, in our experiments we observed that the percent improvement in the *Q*-factor of resonators on which SWNTs were deposited was larger with rougher surfaces than for smoother ones and would also be consistent with the above explanation. Further, presence of flexural resonance modes [16, 17] in thickness shear mode quartz resonators are another potential source of energy dissipation. It can then be surmised that the presence of stiff carbon nanotubes on the surface of the resonator may suppress these out of plane resonance vibrations thereby preventing energy dissipation in this mode and hence causing an increase in the quality factor.

IV. CONCLUSIONS

In this report, we have shown the use of overlayers of SWNTs to increase the *Q*-factor of micromachined miniaturized quartz resonators. The *Q*-factor increased further when the resonators loaded with carbon nanotubes were subjected to vacuum. This was attributed to fact that carbon nanotubes are storehouse of gases, and the desorption of gases reduces the viscoelastic dissipation thereby causing further increase in the *Q*-factor of the resonators. The technique described can be used in conjunction with other techniques, for example, reduction of surface roughness, reduction of support losses by reduction of resonator thickness, making resonator surface convex to increase energy trapping, etc. to increase the *Q*-factor of the resonators even further. Possible phenomenological mechanisms resulting in the observed increase in the *Q*-factor of the resonator have been put forth.

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