Letters

The Effects of Relative Humidity and Reducing Gases on the Temperature Coefficient of Resonant Frequency of ZnO-Based Film Bulk Acoustic Wave Resonator

Xiaotun Qiu, *Student Member, IEEE*, Ziyu Wang, *Student Member, IEEE*, Jie Zhu, *Student Member, IEEE*, Jon Oiler, *Student Member, IEEE*, Rui Tang, Cunjiang Yu, and Hongyu Yu, *Member, IEEE*

***Abstract*—This study describes the influence of relative humidity (RH) and reducing gases on the temperature coefficient of resonant frequency (TCF) of ZnO-based film bulk acoustic wave resonator (FBAR). Upon exposure to moisture or reducing gases, the TCF of FBAR decreased. Water molecules can replace adsorbed oxygen on the ZnO surface. This process was less effective at high temperature, resulting in a lower TCF in high RH. Reducing gases, such as acetone, can reduce the density of ZnO through reaction with the adsorbed oxygen, leading to a lower TCF.**

I. Introduction

Film bulk acoustic wave resonators (FBAR) have been drawing considerable attention both as filters and as high-sensitivity mass sensors in recent years [1], [2]. However, it has been found that the resonant frequency of the FBAR is highly temperature dependent. The temperature coefficient of resonant frequency (TCF) for a conventional Al/ZnO/Al FBAR is about −70 ppm/°C [3]. To reduce TCF, Pinkett *et al.* [4] incorporated a heater in the FBAR to tune its resonant frequency. Wei *et al.* [5] integrated a capacitor in series with the FBAR, which had a temperature coefficient in opposite sign to that of the FBAR's clamped capacitance. Another approach is to obtain temperature-compensated FBARs through a composite arrangement of positive (such as SiO_2) and negative (such as ZnO) TCF materials. With this method, a TCF as low as −0.45 ppm/°C can be achieved.

For a ZnO-based FBAR, the variation of the resonant frequency with temperature is mainly caused by the dependence of the acoustic velocity on temperature. The acoustic velocity is determined by $(E/\rho)^{1/2}$, where E and ρ are the Young's modulus and mass density, respectively. For most materials (such as Al and ZnO), Young's modulus decreases as temperature increases due to the material softening. Although the mass density also decreases with temperature, the acoustic velocity decreases as temperature increases, because of the dominant effect of the Young's modulus, resulting in a negative TCF. Our previous research demonstrated that for ZnO-based FBARs, the surface-adsorbed oxygen had an impact on the acoustic velocity [6]. Other factors, such as relative humidity (RH) [7] and reducing gases [6] can affect the adsorption of oxygen on the ZnO surface. Thus, they can influence the acoustic velocity and consequently, the TCF. These factors need to be considered during the design of FBAR, especially for temperature-compensated devices, which possess very low TCF. In this study, we investigated the effects of RH and reducing gases on the TCF of ZnO-based FBARs. The mechanisms behind these effects were discussed.

Manuscript received April 28, 2010; accepted May 28, 2010.

X. Qiu, J. Zhu, R. Tang, and H. Yu are with School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, AZ (e-mail: xqiu5@asu.edu).

Z. Wang, J. Oiler, and H. Yu are with School of Earth and Space Exploration, Arizona State University, Tempe, AZ.

C. Yu is with School of Mechanical, Aerospace, Chemical and Materials Engineering, Arizona State University, Tempe, AZ.

Digital Object Identifier 10.1109/TUFFC.2010.1637

II. Experimental

The schematic structure of the FBAR is shown in Fig. 1. The FBAR was fabricated on top of a SiN (0.6 μm) diaphragm. A sputtered ZnO film (1.2 μm) was used as the piezoelectric actuation layer. The top and bottom electrodes were made of Au (0.2 μm) and Al (0.2 μm), respectively. The fabrication process of the FBAR was as follows. First, a SiN layer was deposited on a Si wafer (100) with low-pressure chemical vapor deposition (LPCVD). The Si wafer was then etched from the backside anisotropically in potassium hydroxide (KOH) to form the cavity. Next, the bottom Al electrode was deposited by electron-beam (e-beam) evaporation and patterned on top of the SiN film. ZnO was RF sputtered and etched to form the desired pattern. The last step was the e-beam deposition and patterning of the top Au electrode with the lift-off technique. The resulting Au electrode cannot form a conformal coating on the ZnO because of the surface roughness of the film. Thus, there would be some small gaps between ZnO and the electrode. These gaps can provide a channel for the moisture and reducing gases to reach the ZnO.

The FBAR was encapsulated in a chamber to control the RH and gas concentration. An HCC214S hot chuck system (Instec, Inc., Boulder, CO) was employed to adjust the temperature of the FBAR for the TCF measurement. The relative humidity was measured by an HH314A humidity temperature meter (Omega Engineering, Inc., Stamford, CT). The resonant frequency of the FBAR was monitored by an Agilent E5071C network analyzer (Agilent Technologies, Inc., Santa Clara, CA) and recorded with a LabVIEW program (National Instruments Corp., Austin, TX).

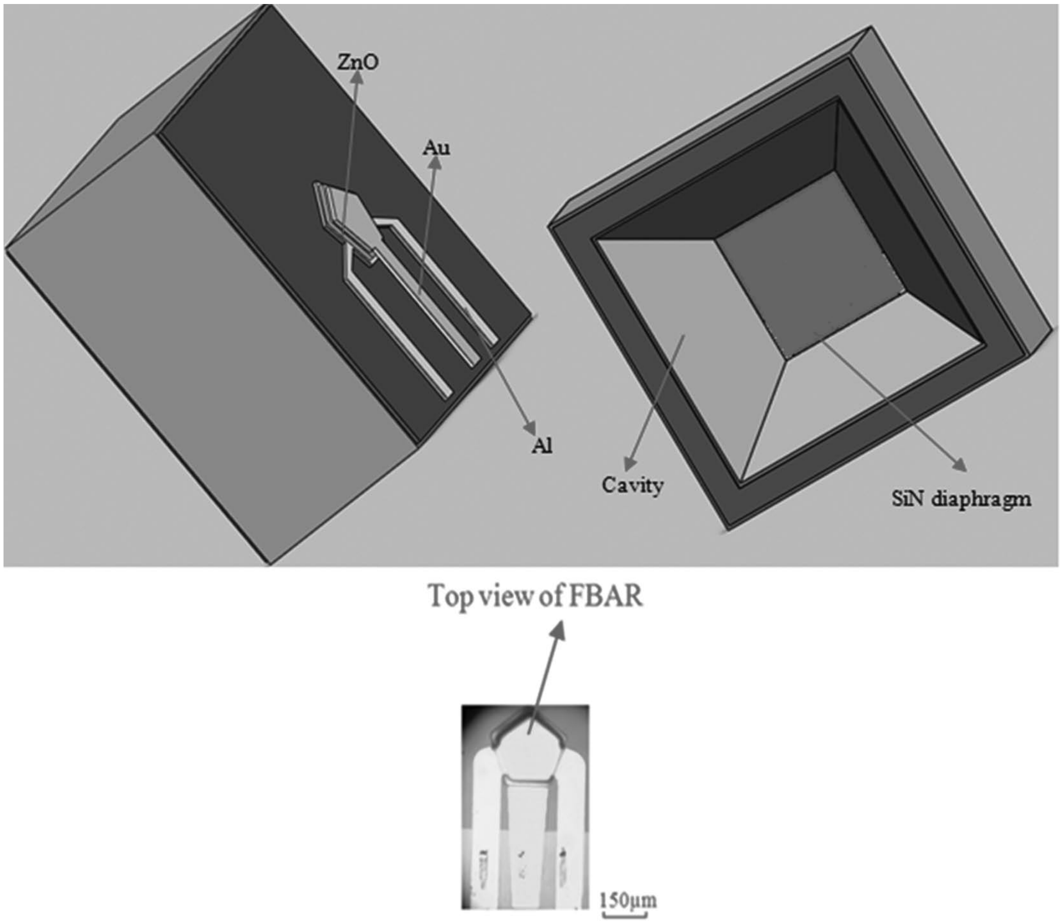

Fig. 1. Schematic structure of the FBAR (top view and bottom view) with a photograph of the top view of a fabricated device.

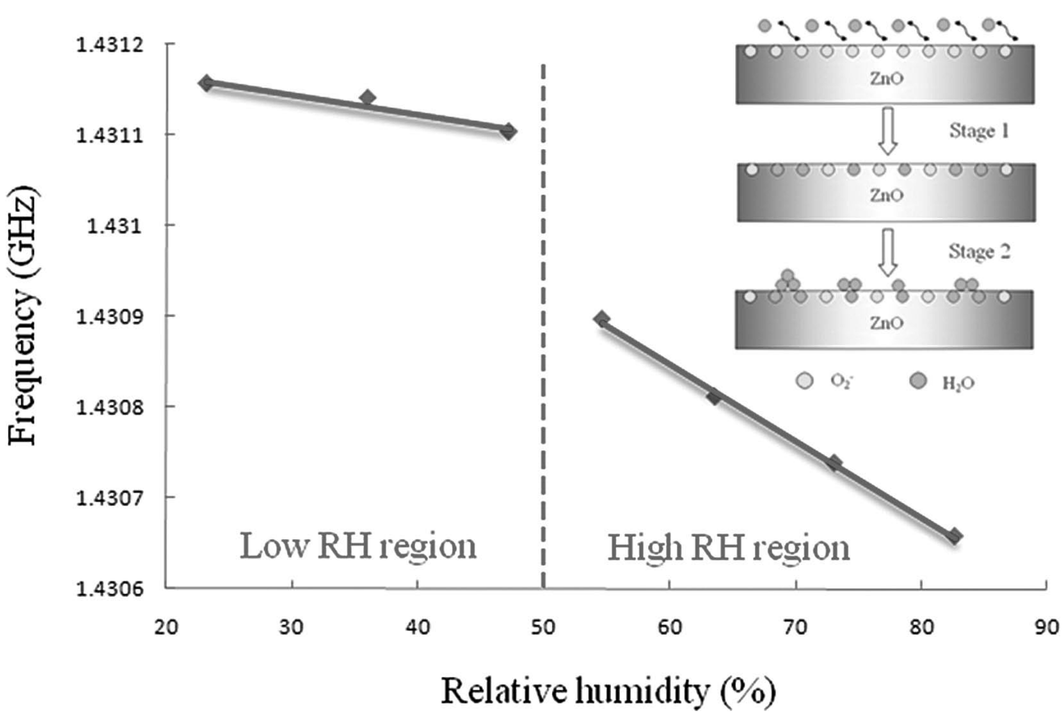

Fig. 2. The RH response of the FBAR at room temperature. Two stages can be identified. At low RH (RH $<$ 50%), a frequency downshift of 2.2 kHz per 1% RH change was observed. At high RH (RH $>$ 50%), a frequency downshift of 8.5 kHz per 1% RH change was obtained. The inset illustrates the mechanism of the two-stage response of the FBAR (the interaction between moisture and the ZnO film was emphasized here without considering the influence of the electrode). At low RH (stage 1), the response was due to the replacement of adsorbed oxygen with water molecules on the ZnO surface. At high RH (stage 2), a discrete water layer began to form on the ZnO surface, which acted as mass loading of the FBAR.

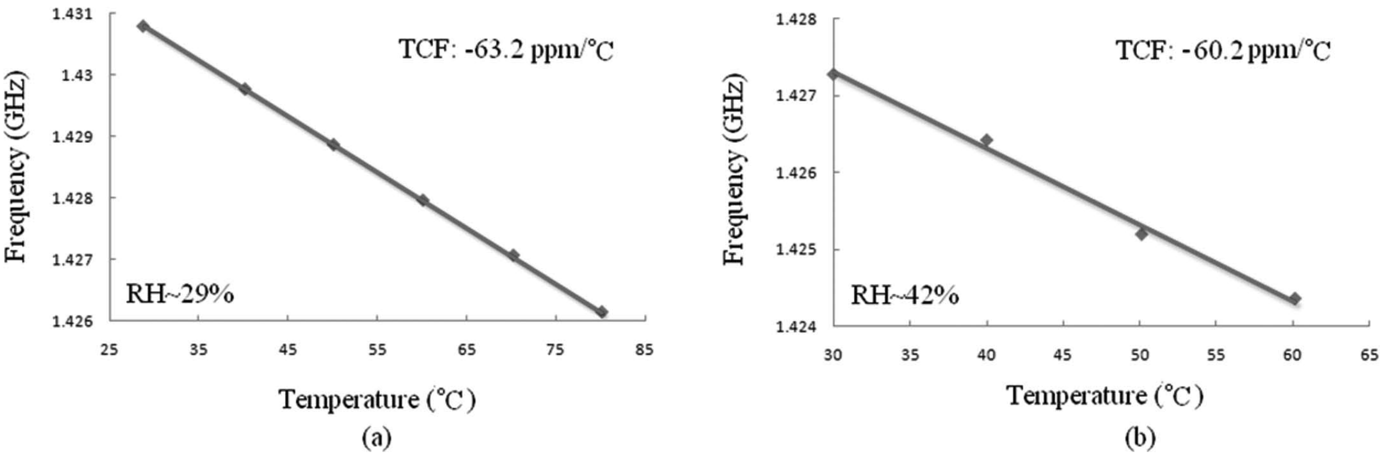

Fig. 3. (a) The decrease of resonant frequency with temperature for the FBAR under normal laboratory conditions (RH ~29%). A TCF of −63.2 ppm/°C was obtained. (b) The temperature response of the FBAR under an average RH of about 42%. A TCF of −60.2 ppm/°C was observed. The highest temperature tested here was 60°C, because as temperature further increased, it was difficult to maintain an average RH of 42%.

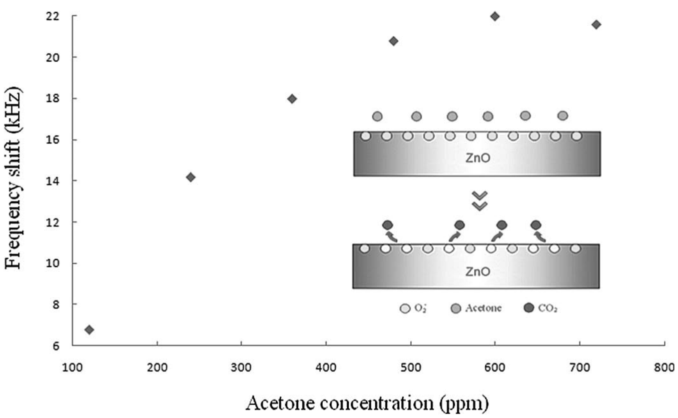

Fig. 4. FBAR's response to acetone: the resonant frequency of the FBAR increased with the acetone concentration. With 120 ppm acetone, the frequency upshift was 6.8 kHz. As the concentration increased to 720 ppm, the frequency upshift increased to 21.6 kHz, reaching saturation. The inset illustrates the sensing mechanism (the interaction between acetone and the ZnO film was emphasized here without considering the influence of the electrode): acetone reacts with the surface adsorbed oxygen ions on the ZnO film and releases CO_2 as a reaction product. Thus, the density of the film decreases, resulting in increase of resonant frequency.

III. Results and Discussion

The resonant frequency of the FBAR was around 1.42 GHz with a noise floor of 0.7 ppm (1 kHz). The quality factor (Q) of the FBAR was between 530 and 550.

The RH response of the FBAR sensor at room temperature is shown in Fig. 2. A two-stage process can be identified based on the different slope values. At low RH (RH $<$ 50%), the resonant frequency decreased linearly with the RH and a frequency downshift of 2.2 kHz per 1% RH change was observed. The RH response in this range was due to the replacement of adsorbed oxygen with water molecules on the ZnO surface [8]. Therefore, the density of the ZnO film increased. The resonant frequency of the FBAR can be determined from the following two equations: $v = (E/\rho)^{1/2}$ and $f = v/2d$, where d is the thickness of the ZnO film, v is the acoustic velocity within the ZnO film, and f is the resonant frequency of the FBAR [6]. As the density of the ZnO film increased with RH, the acoustic velocity decreased, resulting in the decrease of the resonant frequency. At high RH (RH $>$ 50%), the resonant frequency decreased linearly with the RH and a frequency downshift of 8.5 kHz per 1% RH change was obtained. With increasing RH, a discrete water layer began to form on the ZnO surface, which acted as a mass loading of the FBAR. Thus, the resonant frequency of the FBAR decreased linearly with the mass of the water accumulated on top of the resonator [2].

The water layer formed on the ZnO surface when RH was higher than 50% can attenuate the acoustic wave and result in a lower Q [7]. Thus, an RH value less than 50% was selected to monitor its effect on the TCF of FBAR. The temperature response of the FBAR under an average RH of about 42% is shown in Fig. 3(b). A TCF of −60.2 ppm/°C was observed. It was smaller than the TCF (−63.2 ppm/°C) under the normal laboratory conditions (RH ~29%). As mentioned previously, water molecules can replace the adsorbed oxygen on the ZnO film. However, at high temperature, less water can be sustained on the ZnO surface because of its energetically unstable nature [9]. Thus, water will be desorbed from the ZnO film at high temperature, resulting in decrease of the film density. Therefore, the acoustic velocity experienced smaller reduction under high RH, resulting in a lower TCF.

Reducing gases, such as acetone, can react with the oxygen ions on the ZnO film, and release the adsorbed oxygen [10]. Thus, they can affect the TCF of the FBAR. Fig. 4 shows the response of the FBAR to acetone vapor. The resonant frequency of the FBAR increased with the acetone concentration. With 120 ppm acetone, the frequency upshift was 6.8 kHz. As the concentration increased to 720 ppm, the frequency upshift rose to 21.6 kHz, reaching saturation. Acetone reacts with the adsorbed oxygen ions on the ZnO film surface and releases CO_2 as a reaction product [11]. Thus, it can cause the density of the ZnO

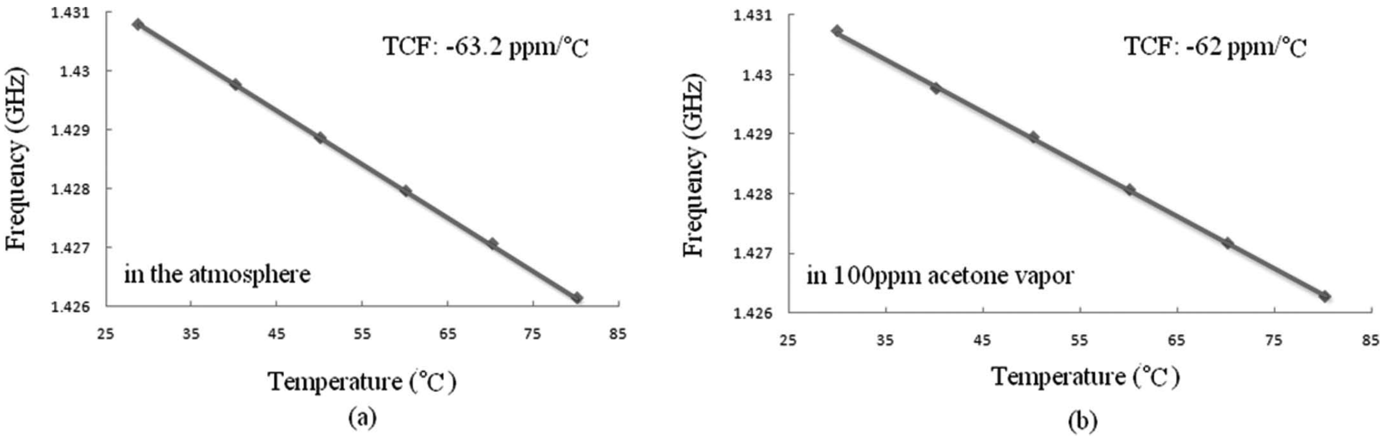

Fig. 5. (a) The decrease of resonant frequency with temperature for the FBAR in the atmosphere. A TCF of −63.2 ppm/°C was obtained. (b) The temperature response of the FBAR in 100 ppm acetone vapor. A TCF of −62 ppm/°C was observed.

film to decrease and result in frequency upshift. The reaction between acetone and the adsorbed oxygen is [11]

$$CH_3COCH_3 + O_2^- \rightarrow CH_3^+ + CH_3O^- + CO_2 + e^-. \quad (1)$$

The temperature response of the FBAR in 100 ppm acetone vapor is shown in Fig. 5(b). A TCF of −62 ppm/°C was observed. It was smaller than the TCF (−63.2 ppm/°C) in the atmosphere. Acetone can react with the adsorbed oxygen ions on the ZnO film to lower the density of the film. As temperature increases, the reaction between acetone and the adsorbed oxygen ions will be enhanced. Thus, the film density will be further reduced. Therefore, the acoustic velocity experienced a smaller reduction in 100 ppm acetone vapor, resulting in a lower TCF. Similar effects can be expected with other reducing gases, such as carbon monoxide.

IV. Summary

In summary, the influence of relative humidity and reducing gases on the TCF of ZnO-based FBARs was investigated. The TCF decreased in high RH or in the presence of reducing gases, such as acetone. The mechanisms behind these effects were discussed. These factors need to be taken into consideration in the future design of FBARs, especially for temperature-compensated FBARs, which possess very low TCF.

References

[1] M. Ueda, M. Hara, S. Taniguchi, T. Yokoyama, T. Nishihara, K. Hashimoto, and Y. Satoh, "Development of an x-band filter using air-gap-type film bulk acoustic resonators," *Jpn. J. Appl. Phys.*, vol. 47, no. 5, pp. 4007–4010, 2008.

[2] H. Zhang and E. S. Kim, "Micromachined acoustic resonant mass sensor," *J. Microelectromech. Syst.*, vol. 14, no. 4, pp. 699–706, 2005.

[3] H. Yu, W. Pang, H. Zhang, and E. S. Kim, "Ultra temperature-stable bulk-acoustic-wave resonators with SiO_2 compensation layer," *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, vol. 54, no. 10, pp. 2102–2109, 2007.

[4] S. L. Pinkett, W. D. Hunt, B. P. Barber, and P. L. Gammel, "Determination of ZnO temperature coefficients using thin film bulk acoustic wave resonators," *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, vol. 49, no. 11, pp. 1491–1496, 2002.

[5] W. Pang, H. Yu, H. Zhang, and E. S. Kim, "Temperature-compensated film bulk acoustic resonator above 2 GHz," *IEEE Electron Device Lett.*, vol. 26, no. 6, pp. 369–371, 2005.

[6] X. Qiu, J. Zhu, J. Oiler, C. Yu, Z. Wang, and H. Yu, "Film bulk acoustic-wave resonator based ultraviolet sensor," *Appl. Phys. Lett.*, vol. 94, no. 15, art. no. 151917, 2009.

[7] X. Qiu, J. Oiler, J. Zhu, Z. Wang, R. Tang, C. Yu, and H. Yu, "Film bulk acoustic-wave resonator based relative humidity sensor using ZnO films," *Electrochem. Solid-State Lett.*, vol. 13, no. 5, pp. J65–J67, 2010.

[8] Y. Takahashi, M. Kanamori, A. Kondoh, H. Minoura, and Y. Ohya, "Photoconductivity of ultrathin zinc oxide films," *Jpn. J. Appl. Phys.*, vol. 33, no. 12A, pp. 6611–6615, 1994.

[9] R. Wang, N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, "Studies of surface wettability conversion on TiO_2 single-crystal surfaces," *J. Phys. Chem. B*, vol. 103, no. 12, pp. 2188–2194, 1999.

[10] C. H. Han, D. W. Hong, S. D. Han, J. Gwak, and K. C. Singh, "Catalytic combustion type hydrogen gas sensor using TiO_2 and UV-LED," *Sens. Actuators B Chem.*, vol. 125, no. 1, pp. 224–228, 2007.

[11] P. P. Sahay, "Zinc oxide thin film gas sensor for detection of acetone," *J. Mater. Sci.*, vol. 40, no. 16, pp. 4383–4385, 2005.