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The effects of temperature, relative humidity and reducing gases on the ultraviolet response of ZnO based film bulk acoustic-wave resonator

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ABSTRACT

This study investigated the influence of temperature, relative humidity and reducing gases on the ultraviolet (UV) response of ZnO based film bulk acoustic-wave resonator (FBAR). As temperature increased, the UV response of the FBAR degraded. This was attributed to the softening of the ZnO film with increasing temperature. Water molecules can replace adsorbed oxygen on the ZnO surface. At high relative humidity, more oxygen was replaced by water. In this way, the density of the ZnO film increased and less oxygen was left on the surface to be desorbed by UV, both of which contributed to a lower UV response. Reducing gases, such as acetone, can react with the surface adsorbed oxygen and reduce the density of the ZnO film, resulting in UV response degradation.

1. Introduction

Detection of ultraviolet (UV) radiation is very important for various commercial and military applications. For example, UV detectors can be used in secure space-to-space communications, pollution monitoring, combustion engineering and early missile plume warning. In the last decade, UV detectors with metal-semiconductor-metal (MSM) structures have been reported extensively. They can be realized either by the ohmic contact photoconductive principle [1] or the Schottky barrier photovoltage principle [2] using ZnO films. ZnO nanostructures have also been employed for UV detecting devices, as they possess single crystal structure characteristics with high surface-to-volume ratio, and have the capability of operating at high temperature and in harsh environments [3,4]. In all of the detectors mentioned above, generally a change in the photogenerated current was measured in the presence and absence of UV illumination. As the UV intensity decreases, the photogenerated current becomes comparable to the dark current, or noise level, resulting in difficulties in measurement. Alternatively, surface acoustic wave (SAW) resonant UV sensors have been developed with photoconductive ZnO film deposited on top of a SAW filter as a UV sensitive layer [5,6].

For ZnO UV detectors, the surface adsorbed oxygen plays an important role in their response to the UV illumination. Different environmental factors, such as temperature, relative humidity (RH) and reducing gases can influence the adsorption of oxygen on the ZnO surface. Thus, they will affect the UV response of the ZnO based detectors. Liao et al. [7] reported the temperature dependence of photoconductivity in single ZnO nanowire. The effects of humidity on the photoresponse of ZnO nanowires were explored by Li et al. [8]. In a previous study, we demonstrated a UV detecting device based on ZnO film bulk acoustic-wave resonator (FBAR) [9]. The resonant frequency of the FBAR increased under UV illumination, which was attributed to the density decrease of the ZnO film through oxygen desorption. In this study, we investigated the effects of temperature, relative humidity and reducing gases on the UV response of the FBAR. These environmental factors need to be taken into consideration during the design and packaging of the sensor to forward it to real life applications.

2. Experimental

The schematic structure of the FBAR UV sensor and its UV response are 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 both as the UV sensitive layer and the piezoelectric actuation layer for the FBAR sensor. 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

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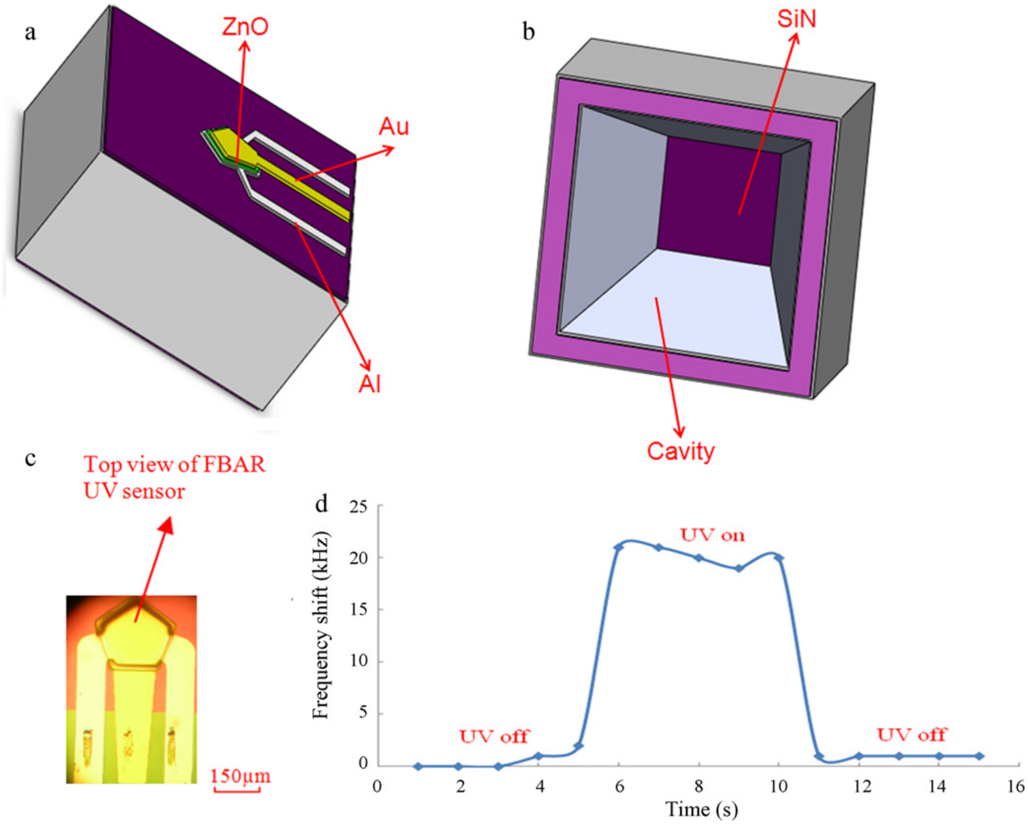

Fig. 1. Schematic structure of the FBAR: (a) top view; (b) bottom view; (c) a photograph of the top view of a fabricated device; (d) UV (600 μW/cm^2) response of the FBAR sensor. A frequency upshift of 19 kHz was observed.

on a Si wafer (1 0 0) with low-pressure chemical vapor deposition (LPCVD). Then the Si wafer was 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 radio-frequency (RF) sputtered and etched to form the desired pattern. The last step was the e-beam deposition and patterning of top Au electrode by lift-off.

A versatile hand-held ultraviolet lamp (365 nm, Cole-Parmer, Vernon Hills, IL) was used as the UV source. A UVX digital ultraviolet intensity meter (Cole-Parmer, Vernon Hills, IL) was applied to calibrate the UV power received by the FBAR sensor. A HCC214S hot chuck system (INSTEC, Boulder, CO) was employed to adjust the temperature of the FBAR. The sensor was encapsulated in a chamber to control the RH and gas concentration. The humidity was measured by a HH314A humidity temperature meter (OMEGA, Stamford, CT). The resonant frequency of the FBAR was monitored with an Agilent E5071C network analyzer (Agilent, Santa Clara, CA) and recorded by a LabVIEW program (National Instruments, Austin, TX). It had a noise floor of 0.7 ppm at 1.4 GHz, which was suitable for integration with a wireless sensor network. The quality factor (Q) of the FBAR was between 550 and 570.

3. Results and discussion

The inset of Fig. 1 shows the frequency response of the FBAR sensor under UV illumination (600 μW/cm^2). A frequency upshift of 19 kHz was observed (20 °C). The resonant frequency of the FBAR can be determined from the following two equations:

$$v = \sqrt{\frac{E}{\rho}} \tag{1}$$

$$f = \frac{v}{2d} \tag{2}$$

where E, ρ and d are the elastic modulus, density and thickness of the ZnO film, respectively. The variable v represents the acoustic velocity within the ZnO film and f is the resonant frequency of the FBAR. The frequency upshift was due to the density decrease of the ZnO film upon UV illumination. It is well established that when UV light is incident, electron–hole pairs are generated inside the ZnO film. The holes produced by light absorption migrate to the surface and discharge the negatively charged adsorbed oxygen ions. When an oxygen ion is discharged by the capture of a hole, it will be thermally desorbed. In this way, the density of the ZnO film will decrease, resulting in the increase of acoustic velocity inside the film. Therefore, the resonant frequency of the FBAR sensor will increase. When UV light is absent, oxygen readsorption will occur. Consequently, the density of the ZnO film will increase and the resonant frequency of FBAR will decrease accordingly [9].

Fig. 2(a) shows the shift of resonant frequency with temperature for the FBAR sensor. A temperature coefficient of resonant frequency (TCF) of −63.2 ppm/°C was obtained. For the ZnO based FBAR, the variation of the resonant frequency with temperature is mainly due to the dependence of the acoustic velocity on temperature. 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, owing to the dominant effect of the Young's modulus, resulting in a negative TCF.

In Fig. 2(b), the UV response (600 μW/cm^2) of the FBAR sensor under different temperatures was illustrated. As the temperature increased from 25 °C to 32 °C, the frequency upshift decreased from 18.2 kHz to 17.4 kHz. It further decreased to 16.6 kHz and 15.8 kHz when the temperature reached 39.6 °C and 44.9 °C. As mentioned

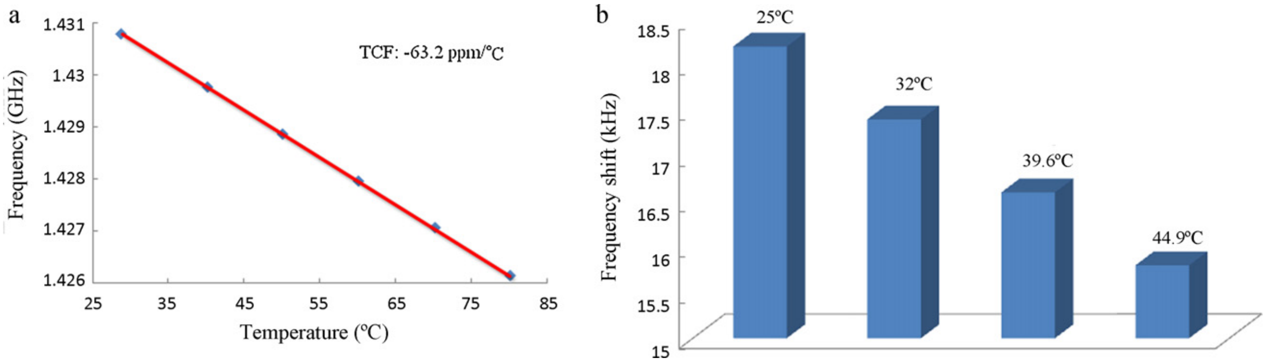

Fig. 2. (a) The shift of resonant frequency with temperature for the FBAR sensor. A temperature coefficient of resonant frequency (TCF) of −63.2 ppm/°C was obtained; (b) the UV response (600 μW/cm^2) of the FBAR sensor under different temperatures. At 25 °C, the frequency upshift was 18.2 kHz. At 32 °C, the frequency upshift decreased to 17.4 kHz. It further decreased to 16.6 kHz and 15.8 kHz when the temperature reached 39.6 °C and 44.9 °C. For higher temperatures, the noise floor of the FBAR increased, resulting in difficulties in measuring the exact UV response of the sensor.

before, ultraviolet radiation can generate electron–hole pairs in the ZnO film. The holes produced can migrate to the surface and discharge the negatively charged adsorbed oxygen ions, resulting in oxygen desorption from the ZnO film. With the same UV intensity, the amount of oxygen desorbed remains almost the same, which means the density decrease $\Delta\rho$ induced by UV is constant at different temperatures.

The shift of resonant frequency Δf due to UV illumination can be formulated as following:

$$\Delta f = \frac{1}{2d}\left(\sqrt{\frac{E}{\rho-\Delta\rho}} - \sqrt{\frac{E}{\rho}}\right) = \frac{\sqrt{E}}{2d}\,\frac{(1-\sqrt{1-(\Delta\rho/\rho)})}{\sqrt{\rho-\Delta\rho}} \tag{3}$$

In the above equation, ρ » $\Delta\rho$. In this way:

$$\Delta f \approx \frac{\sqrt{E}}{2d}\,\frac{(1-1+(1/2)(\Delta\rho/\rho))}{\sqrt{\rho}} = \frac{\sqrt{E}}{4d\rho\sqrt{\rho}}\Delta\rho \tag{4}$$

As temperature increases, the Young's modulus of ZnO decreases. Therefore, a smaller frequency upshift can be expected at high temperature if we assume the density of the ZnO film does not change in the experiment temperature range (from 25 °C to 45 °C).

Frequency upshift was observed previously by Sharma et al. [10] in their SAW UV sensor which utilized a ZnO/fused quartz SAW delay line. An alternative explanation was proposed stating that the change of the elastic modulus of the ZnO film (ΔE) due to UV stiffening was the main reason for the frequency upshift. However, UV stiffening cannot be used to explain the phenomena shown in Fig. 2(b).

The shift of resonant frequency Δf due to UV stiffening is as follows:

$$\Delta f = \frac{1}{2d}\left(\sqrt{\frac{E+\Delta E}{\rho}} - \sqrt{\frac{E}{\rho}}\right) = \frac{\sqrt{E}}{2d}\,\frac{(\sqrt{1+(\Delta E/E)}-1)}{\sqrt{\rho}} \tag{5}$$

In the above equation, E » ΔE. In this way:

$$\Delta f \approx \frac{\sqrt{E}}{2d}\,\frac{(1+(1/2)(\Delta E/E)-1)}{\sqrt{\rho}} = \frac{\Delta E}{4d\sqrt{\rho E}} \tag{6}$$

With the same UV intensity, the stiffening effect is the same at different temperatures. However, a smaller E occurs at high temperature. If UV stiffening is the main reason for the frequency upshift, it will result in an enhanced UV response (assuming constant ZnO density in the experiment temperature range). In contrast, in our experiment, a lower UV response was observed. Thus, UV stiffening can be ruled out as the main reason for the frequency upshift obtained in the FBAR sensor.

Fig. 3(a) shows the frequency response of the FBAR sensor to different RH. A two-stage process can be identified based on the different slope values [11]. 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, 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 on the FBAR. Thus, the resonant frequency of the FBAR decreased linearly with the mass of the water accumulated on top of the resonator [12].

The UV (600 μW/cm^2) response of the FBAR sensor in different RH is shown in Fig. 3(b). With 23.2% RH, a frequency upshift of 19 kHz was obtained. As RH increased, the frequency upshift decreased. With 35.8% RH, the frequency upshift was 18.4 kHz and it further decreased to 16.6 kHz as the RH increased to 54.5%. As the RH continued to rise, the discrete water layer formed on the ZnO surface degraded the Q of the FBAR (due to the attenuation of acoustic wave in the water layer) [11], resulting in a large noise floor which prevented measuring the exact UV response of the sensor. As mentioned above, water molecules can take the place of adsorbed oxygen on the ZnO surface. Thus, the density of the ZnO film increases at high RH. At the same time, as adsorbed oxygen is replaced by water, there is less oxygen left on the ZnO surface to be desorbed by UV. In this way, the density change induced by UV illumination decreases, resulting in a lower UV response at high RH.

Reducing gases, such as acetone, can react with the oxygen ions on the ZnO film, and release the adsorbed oxygen [13]. Thus, they can affect the UV response of the FBAR. Fig. 4(a) 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. Previous study demonstrated that acetone and UV light shared a similar mechanism to upshift the frequency of the FBAR sensor [9]. It reacts with the adsorbed oxygen ions on the ZnO film surface and releases CO_2 as a reaction product [14]. Thus, acetone can cause the density of the ZnO film to decrease and result in an increase of resonant frequency.

In the presence of acetone, it reacted with some surface adsorbed oxygen ions on the ZnO film. Therefore, when UV light was incident, there was less oxygen left on the surface to be desorbed by UV. Thus, the density change will become smaller with the same UV intensity, followed by a smaller frequency upshift. Fig. 4(b)

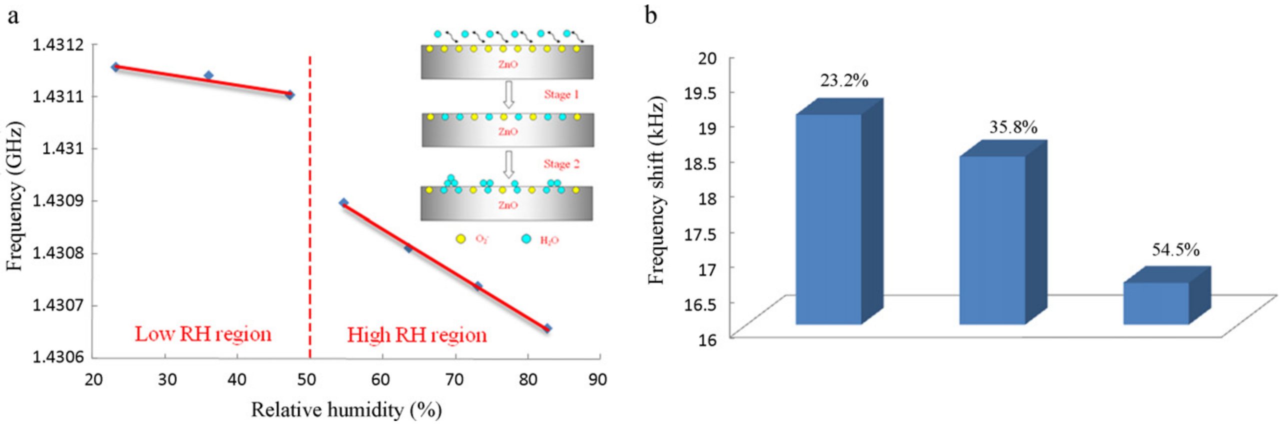

Fig. 3. (a) The RH response of the FBAR at room temperature. Two stages can be identified. At low RH (RH < 50%), a frequency downshift of 2.2 kHz per 1% RH change was observed. At high RH (RH > 50%), a frequency downshift of 8.5 kHz per 1% RH change was obtained. The inset illustrated the mechanism of the two-stage response of the FBAR. 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 a mass loading on the FBAR; (b) the UV (600 μW/cm^2) response of the FBAR sensor under different RH. With 23.2% RH, a frequency upshift of 19 kHz was obtained. As RH increased, the frequency upshift decreased. With 35.8% RH, the frequency upshift was 18.4 kHz and it further decreased to 16.6 kHz as RH increased to 54.5%.

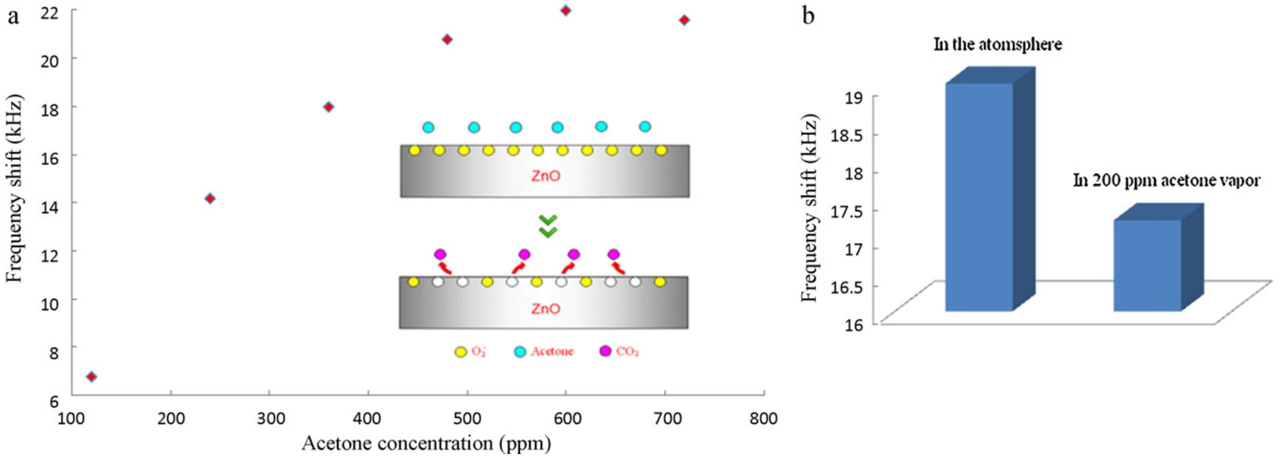

Fig. 4. (a) FBAR's response to acetone: the resonant frequency of the FBAR increased with the acetone concentration. With 120 ppm acetone, the frequency upshift was 6.8 kHz. As the concentration increased to 720 ppm, the frequency upshift rose to 21.6 kHz, researching saturation. The inset illustrated the sensing mechanism: 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 an increase of resonant frequency; (b) the frequency upshift of the UV illuminated FBAR sensor in the atmosphere and in 200 ppm acetone vapor. It showed that in an acetone filled environment, the UV (600 μW/cm^2) response was degraded (17.2 kHz compared to 19 kHz in the atmosphere).

shows the UV response of the FBAR sensor in the atmosphere and in 200 ppm acetone vapor. It illustrated that in an acetone filled environment, the UV (600 μW/cm^2) response was degraded (17.2 kHz compared to 19 kHz in the atmosphere). Similar effects can be expected with other reducing gases, such as carbon monoxide.

4. Conclusion

In conclusion, the effects of temperature, relative humidity and reducing gases on the UV response of ZnO based FBAR was investigated. As temperature and relative humidity increased, the UV response of the FBAR degraded. Reducing gases, such as acetone, were also able to degrade the UV sensitivity of the FBAR. The mechanisms behind these effects were discussed. In future applications, a vacuum package may need to be pursued for the FBAR UV sensor to eliminate the influence of these environmental factors.

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