Thermal annealing effect on ZnO surface acoustic wave-based ultraviolet light sensors on glass substrates

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Surface acoustic wave (SAW) based ultraviolet (UV) light sensors have a high sensitivity, and have been extensively studied and explored for application. However all of them were made of piezoelectric (PE) bulk materials or PE thin films on crystalline substrates such as Si and sapphire. This paper reports the fabrication of ZnO thin film SAW UV-light sensors on glass substrates and the effect of post-deposition thermal annealing on the sensing performance. It was found that annealing at temperatures higher than 300 °C can improve the properties of ZnO films and the sensing performance of the UV-sensors remarkably. When the ZnO film annealed at 400 °C was used for sensors, the UV light induced resonant frequency shift increased more than 20 times with the response speed reduced to less than 2.4 sec, much better than those made on ZnO films with lower temperature annealing.

ZnO is a direct band gap semiconductor and possesses many desirable electronic, piezoelectric and optical properties, enabling its application in various areas such as nano-generators1, light emitting diodes2, solar cells3 and sensors etc. ZnO has an energy band gap of 3.37 eV, and can absorb ultraviolet (UV) light with high absorption coefficient. This has
been utilized to develop high sensitivity UV light sensors\textsuperscript{4-6}. Surface acoustic wave (SAW) devices with ZnO sensing layers have been used to develop SAW-based UV sensors\textsuperscript{7,8}. Pang et al reported a Love wave mode ZnO/LiTaO\textsubscript{3} SAW UV light sensor, and achieved a high sensitivity of \(~150\) kHz frequency shift under a 350 \(\mu W//cm^2\) UV light exposure\textsuperscript{9}. Peng et al developed LiNbO\textsubscript{3}-based SAW sensors with ZnO nanowires as the sensitive layer, and demonstrated a better sensitivity than those with a sputtered ZnO film\textsuperscript{10}. Wei et al fabricated ZnO SAW UV sensors on Si substrates and showed that thin film ZnO SAW UV sensors also have very good performance\textsuperscript{11}.

However, all of the SAW UV sensors were made of piezoelectric (PE) bulk materials or PE thin films on crystalline substrates such as Si and sapphire. Recently we have successfully developed a transparent SAW on ZnO/glass technology, and demonstrated the high performance of the devices and their potential applications in sensors\textsuperscript{12}. SAW devices on glass are cheap, and can be used as a transparent sensor array for multiple passive wireless sensing applications on windows and screens of electronic devices and systems etc. For the transparent SAW devices on glass, light could get into the devices from both sides of the devices with no blockage of light, and this may find more applications for SAW UV sensors. Here we report the fabrication of high sensitivity of ZnO/glass SAW UV-light sensor and the effect of thermal annealing on the performance of UV-light sensing.

ZnO PE thin films were deposited on 4 inch glass substrates (Corning 2318) using direct current (DC) magnetron sputtering. A 99.99\% Zinc target was used for sputtering in a mixture gas of Ar/O\textsubscript{2} at a ratio of 100/50 (sccm). The deposition conditions had been optimized previously\textsuperscript{13} and were used directly in this work. The deposition conditions were: 1 Pa deposition pressure, 75 V bias voltage and 200 W deposition power. The films were deposited without intentional heating, but a rise of temperature to about 65 \(^\circ\)C was observed due to ion bombardment. The ZnO thickness was 2.0 \(\mu m\) for all the devices used in this work. After deposition, rapid thermal annealing (RTP CT-100M, Premtek) in nitrogen (N\textsubscript{2}) atmosphere was implemented to reduce defects and stress in the films with annealing temperature, \(T_A\), varied from 200, 300 to 400 \(^\circ\)C for a fixed duration of 10 mins. The heating rate was 10 \(^\circ\)C/s, while it was naturally cooled down under a N\textsubscript{2} flow rate of 1 l/min. Crystal structure was characterized using scanning electron microscope (SEM, Hitachi S-4800), atomic force microscope (AFM) (SPI-3800N, Seiko Co.) and X-Ray diffraction (Panalytical Empyrean).
Aluminum (Al) interdigitated transducers (IDT) with a periodicity of 12 μm (i.e. the wavelength, \( \lambda \)) were fabricated by standard UV photolithography and lift-off process. An Al layer of \(~80\) nm thickness was deposited by thermal evaporation. The IDTs have 30 pairs of fingers and 10 pairs of reflective gratings. The acoustic aperture is 4000 μm and the distance between the two IDTs is \(20 \lambda\).

An Agilent E5071C network analyzer was used to characterize the SAW devices, which was controlled by a LabVIEW-based measurement program. A UV lamp (ANUP 5252, Panasonic) with a 365 nm monochromator was used as the UV light source. The UV intensity was measured by a UV-optometer (SUSS). All UV sensor characterization and UV detection were implemented at a temperature of \(20 \pm 1\) °C, which was controlled during the experiments.

Fig. 1(a) shows an SEM image of the cross sectional ZnO film after 400 °C annealing. The ZnO nano-columns are tightly packed, perpendicular to the substrate. The roughness of the film surface is 6.8 nm measured by AFM as shown in Fig. 1(b), showing a good surface smoothness, particularly important for planar structure device fabrication. Fig. 1(c) shows the XRD curves of the ZnO films annealed at different temperatures, \(T_A\). The XRD curves showed a single peak around at 34.3°, corresponding to the ZnO (0002) crystal orientation. The peak shifted from 34.30° of the as-grown sample, to 34.38° of the sample annealed at 400 °C, close to the value of the standard ZnO powder (34.4220°). The deviation of the XRD peak from the standard value is caused by the stress in the film and was utilized to estimate the internal stress of the films for this work. The stress was roughly \(-1.49\) GPa for the as-deposited ZnO thin film, and reduced to \(-250\) MPa after annealing at 400 °C, consistent with the observation reported in ref.[16]. The full-width at half maximum (FWHM) for (0002) ZnO peak were 0.201°, 0.194°, 0.193° and 0.190° for the as-deposited sample and those annealed at 200, 300 and 400 °C, respectively, (hereafter they are designated as S1, S2, S3 and S4, respectively). The grain size of the ZnO films estimated using the Debye–Scherrer formula is shown in Fig. 1(d), increased from 43.3 nm to 45.7 nm when \(T_A\) was increased from room temperature to 400 °C, showing the same tendency as that of the ZnO films on Si substrates.

The reflection (S11) and transmission (S21) spectra of the SAW devices were characterized. The one with 400 °C annealing showed the best transmission properties as illustrated in Fig. 2. A strong Rayleigh resonant peak can be seen at 211.6 MHz. The insertion loss is about –25.0 dB and the signal amplitude is approximately 30 dB. The corresponding acoustic
velocity \( (\nu = \lambda f) \) is 2540 m/s, close to 2650 m/s reported for single crystalline ZnO material. The effective electromechanical coupling coefficients, \( k^2 \), increased from 1.09 % to 1.87 % with the increase of \( T_A \), comparable to those of the ZnO SAW devices on Si and ZnO film bulk acoustic resonators. The increase of \( k^2 \) further indicates that thermal annealing can significantly improve the property of ZnO films and SAW devices. All the above results show the SAW devices on glass substrates work well once having a proper thermal annealing.

Illumination of UV light on ZnO layer can generate free electron-hole pairs and they are confined in the surface layer of the ZnO film owing to the large absorption coefficient \( (10^4 \sim 10^5 \text{ cm}^{-1}) \), inducing a change in resonant frequency and insertion loss of the SAW devices. Defects in the middle band gap may also respond to long wavelength light, but our devices showed a good visible-light blind property, and did not respond with a noticeable frequency shift as those observed under UV light illumination. The responses of the frequency and insertion loss to UV light are shown in Fig. 3. The UV light intensity was 7.6 mW/cm². When the UV light was exposed on the SAW device, the resonant frequency decreased and the insertion loss increased for all the devices. It can be seen that annealing at 400 °C improved the UV response significantly. For Sample S1 and S2, a frequency shift of only 3.5 kHz and an insertion loss shift of -0.001 dB were observed. The shift became stronger with the increase of \( T_A \), the frequency and insertion loss shift of Sample S4 were more than 70 kHz and -3 dB, respectively (note there is a break line in the y-axis of Fig. 3 for easy inclusion and reading of all the curves).

It is interesting to note the difference in the initial and the second response curves in Fig. 3 when the light was switched on. For Sample S1-S3, the frequency shift (absolute amplitude, same for the following discussions) gradually increased with a delay time of 20~30 sec when the light was switched on repeatedly, while that of S4 gradually increased with a similar delay time for the first pulse of light. When the light was switched on again, the response became instantaneous (less than ~2.4 sec, limited by the time interval required for one sweeping measurement) and then the frequency shift gradually decreased, opposite to that for the first light pulse. Absorbed water and oxygen on the surface may be responsible for the delay of the response (or the tail). Since they were all measured at the same conditions, the possible cause by desorption of the water and oxygen on the surface for S4, thus, can be ruled out. Deep level defects or surface states are believed to be responsible for the strange behavior. When the light is on, electrons or holes trapped in deep defects and surface states are released gradually, causing the delay of the response due to the change of surface
conductivity or capacitance. When the light is off, the defects and surface state are filled with electrons gradually, inducing an opposite effect to the initial response. To clarify this, we conducted the same measurement by keeping the sensor in dark for different durations as shown in Fig. 4. For up to 450 s in dark, the frequency shift decreased when the light was on. After keeping the sensor in dark for 750 s, the frequency shift at light on had the same response behavior as the first light pulse, implying the deep defects or surface states are likely the cause for the opposite response of the frequency shift observed. However it is difficult to distinguish whether it is caused by defects or surface states, and detailed investigation is ongoing.

UV light sensing at different light intensities were carried out and the results are shown in Fig. 5. The frequency down shift increases from ~10 kHz to ~65 kHz when the light intensity was increased from 0.1 to 7.6 mW/cm². Meanwhile the insertion loss increases from -0.25 dB to nearly -2.5 dB. Fig. 5(c) shows the frequency shift and insertion loss as a function of light intensity. They increase linearly with the light intensity, and show a tendency of saturation at high light intensity. It was reported this is caused by the saturation of photo-carrier generation, consistent with our observation.

In conclusion, we have fabricated ZnO/glass SAW devices and investigated the effect of annealing temperature on the performance of the UV light sensors. It showed that ZnO/glass SAW devices have high transmission properties, and thermal annealing at 400 °C could improve UV sensing performance significantly with the sensitivity comparable to those made of piezoelectric bulk materials, demonstrated a good potential for UV sensor application.

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References

Figure captions

FIG. 1. Characterization of ZnO deposited on glass. An SEM image of the cross-section (a), an AFM image of the surface (b), an XRD curve of the ZnO annealed at 400 °C (c), and grain size and XRD peak angle as a function of $T_A$ (d).

FIG. 2. Reflection ($S_{11}$) and transmission ($S_{21}$) spectrum of the device with 400 °C annealing.

FIG. 3. Response of frequency (a) and insertion loss (b) of the SAW devices annealed at different temperatures under a fixed intensity (7.6 mW/cm²) of UV light illumination.

FIG. 4. Frequency response of S4 to UV light illumination when the sensor was kept in dark for different durations. The light intensity was 7.6 mW/cm².

FIG. 5. Frequency shift (a) and insertion loss (b) at different UV intensities, and their shifts (c) as a function of UV light intensity. The 400 °C annealed ZnO sensor (S4) was used for this experiment.