RF sputtered piezoelectric zinc oxide thin film for transducer applications

Yu-Hsiang Hsu · John Lin · William C. Tang

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Abstract This paper demonstrates the substrate dependency of the c-axis zinc oxide growth in radio-frequency sputtering system. Different deposition conditions were designed to study the influences of Si, SiO$_2$/Si, Au/Ti/Si, and Au/Ti/SiO$_2$/Si substrates on the piezoelectric and crystalline qualities of the ZnO thin films. Experimental results showed that the multilayer of Au/Ti/SiO$_2$/Si-coated silicon substrate provided a surface that facilitated the growth of ZnO thin film with the most preferred crystalline orientation. The 1.5 µm-thick thermally grown amorphous silicon dioxide layer effectively masked the crystalline surface of the silicon substrate, thus allowing the depositions of high-quality 20 nm-thick titanium adhesion layer followed by 150 nm-thick of gold thin film. The gold-coated surface allowed deposition of highly columnar ZnO polycrystalline structures. It was also demonstrated that by lowering the deposition rate at the start of sputtering by lowering RF power to less than one-third of the targeted RF power, a fine ZnO seed layer could be created for subsequent higher-rate deposition. This two-step deposition method resulted in substantially enhanced ZnO film quality compared to single-step approach. The influence of stress relaxation by annealing was also investigated and was found to be effective in releasing most of the residual stress in this layered structure.

1 Introduction

Zinc Oxide (ZnO) is a material that possesses versatile mechanical, electrical, chemical, and optical properties. Because of its unique physical properties, ZnO has drawn broad attentions in different fields and been utilized in a wide range of applications. In particular, using piezoelectric ZnO thin films to design sensors and actuators has been studied with demonstrated results, including surface acoustic wave (SAW) device, acousto-optical device, acoustic microscopy, electromechanical filters, and bulk acoustic wave (BAW) devices [1]. A strategic advantage of deposited ZnO thin film is that it is amenable to be integrated with IC fabrication process, enabling a single-chip system of the transducers with signal processing electronics.

The performance of piezoelectric sensors and actuators critically depends on the quality of the piezoelectric ZnO thin films. Substantial research efforts have been devoted to the studies of various deposition methods and parameters for ZnO thin films during the last two decades. Among various approaches, RF sputtering is the most studied, and is the method used in this research. The deposition parameters that could influence the quality of the resulting films include RF power, the ratio of argon to oxygen as the feed gases, target-to-substrate distance, deposition temperature and pressure, substrate, and post-deposition annealing temperature. To achieve a ZnO thin film with high piezoelectric effect, the polycrystalline structures within the thin film should exhibit a strong dominance of c-axis orientation. In particular, high deposition rates usually result in randomized polycrystalline structures within the thin film, and thus compromising piezoelectric performance. It has been reported that the deposition rate should therefore be limited to 1 µm/h (16 nm/min) [2], which in

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turn is more effectively modulated by the RF power than any other deposition conditions. On the other hand, the ratio of the two feed gases, argon and oxygen, affects the stoichiometry of the resulting film. A higher concentration of oxygen atoms in the deposition system usually results in close to stoichiometric ZnO films, which otherwise would be rich in Zn [3]. One of the characteristics of Zn-rich ZnO films is lower electrical resistivity than that of stoichiometric ones. A higher oxygen content, however, would suppress deposition rate [4], [5]. At the same time, increasing the target-to-substrate distance would increase the deposition rate and lower the resistivity of the result film, exhibiting effects similar to lower oxygen content [4]. This could be explained by the increased collisions of sputtered ZnO molecules along the path from the sputtering target to the substrate, and thus promoting pyrolysis into individual Zn and O atoms. This could be compensated by providing a higher concentration of oxygen in the plasma to enhance the stoichiometry. Another factor influencing deposition rate, and indirectly the film quality, is substrate temperature. A higher substrate temperature would result in lower deposition rate [4], and at temperature exceeding 150 °C the film quality would be compromised [6]. The most optimum substrate temperature has been found to be 100 °C. Also, a higher deposition pressure would enhance the preferred-orientation of ZnO while forming large crystalline structures with roughened surface topology [7]. Since ZnO is deposited at an elevated temperature, considerable residual stress is accumulated after deposition and cooling to room temperature, which affects the mechanical and electrical properties of the resulting films. Postdeposition annealing at 400 °C for an hour could effectively relax the residual stress of ZnO films sputtered on these four different substrate and improve the film quality [8].

The most important parameter determining the quality of the sputtered ZnO thin film is the substrate on which the film is deposited. Various substrates had been used in different studies but their influences on the film quality were not clearly identified. In [9], a study was conducted comparing the qualities of different ZnO thin films sputtered on glass, (100) silicon, silicon nitride (Si₃N₄), borosilicate glass (BSG), aluminum (Al), and chromium (Cr). The important finding was that the amorphous substrates such as glass, BSG, and Si₃N₄, could produce high quality ZnO films. Other studies focused on metalized silicon surfaces and the role of the adhesion layer for noble metals on silicon. It was found that titanium (Ti) could form a better ZnO film than Cr as the adhesion layer for gold (Au) [10]. Also, platinum (Pt) was a good surface for ZnO growth, and a thin layer of Pt on Al could form a high quality ZnO film.

In the present study, it will be shown that layered substrate can promote the formation of the c-axis oriented polycrystalline structures within the sputtered ZnO thin film. By comparing the differences among Si, SiO₂/Si, Au/Ti/Si, and Au/Ti/SiO₂/Si substrates, it had been experimentally demonstrated that a high quality c-axis ZnO thin film could be achieved with layered Au/Ti/SiO₂/Si configurations. To improve the film quality further, two-step deposition was studied and demonstrated to be effective [7]. With two-step deposition and Au/Ti/SiO₂/Si substrate, a highly c-axis oriented and well-aligned ZnO thin film has been realized and verified with X-ray Diffractometer (XRD) and images taken from scanning electron microscopy (SEM).

2 Experimental studies

The ZnO films in this work were deposited with a PERKIN-ELMER 2400-8SA RF planar magnetron sputtering system. The ZnO target was 8 inch in diameter with 99.99% purity. The system is equipped with a 21.5 inches rotating water-cooled annular table that controls and maintains the substrate temperature during deposition. Different argon-to-oxygen ratio could be manipulated by controlling the flow rate of each gas with roller meters. Deposition pressure was controlled by combinations of flow rate, throttle, and MKS Type 250 Gas Pressure/Flow Controller controlled needle valves. Table 1 shows the optimal deposition parameters that had been characterized specifically for this sputtering system. The resulting films were studied for their c-axis orientation contents with XRD, and the surface topology and film defects were investigated with SEM.

2.1 Design of experiments

A set of experiments was designed to study the effects of layered substrates and the two-step deposition as the two major influencing factors on the quality of the sputtered ZnO thin film. To minimize variations from deposition to deposition processes, ZnO was sputtered simultaneously during each experiment on the four types of substrate surfaces, native (100) silicon (Si), thermally grown silicon

<table>
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<th>Table 1 Characterized optimal parameters for ZnO deposition</th>
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<tr>
<td>RF Power</td>
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<td>Ar:O ratio</td>
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<td>Target-to-substrate distance</td>
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<td>Deposition temperature</td>
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dioxide over Si (SiO$_2$/Si), gold with titanium as adhesion layer over Si (Au/Ti/Si), and gold with titanium over oxidized silicon (Au/Ti/SiO$_2$/Si). The metal films were deposited simultaneously on both Si and SiO$_2$/Si surfaces in an Airco/Temescal CV-8 E-beam evaporator. The thicknesses of the SiO$_2$, Au, and Ti were 1.5 μm, 150 nm, and 20 nm, respectively. Each square sample measured 1.5 cm on a side, which was sufficiently small to minimize substrate bowing resulting from mismatches in thermal expansion coefficients between the sputtered ZnO films and the substrates [11]. The deposition conditions were kept the same for all samples and was detailed in Table 1 with the exceptions of the RF power levels and the argon-to-oxygen (Ar:O) ratios. Table 2 shows the six different deposition conditions in this study. A 10 min pre-sputtering step was performed for all six sets of experiments with 100% Ar flowing at 69 sccm pumped to 17 mtorr. The pre-sputtering RF power level for each experiment was set according to Table 2. This pre-sputtering step served to clean the target while allowing sufficient time for the vapor pressures and the plasma to stabilize inside the chamber. The main deposition duration was fixed at 2 h for all experiments to achieve comparable thicknesses for the resulting ZnO films.

During the course of the study, it was observed that the optimal Ar:O ratio for our particular sputtering system is 100% Ar. The two-step depositions in this research were performed by starting the RF power at 100 W in the pre-deposition step for a duration of 1 min for experiments T2 to T5, and 5 min for T6. For these five set of experiments, a high quality seed layer was deposited at a slow rate on the substrate prior to the main deposition steps. Substrate dependency was studied under three different deposition conditions T3, T4, and T5. Finally, the effectiveness of post-deposition annealing on stress relaxation was investigated with AG Heat pulse 2146 Rapid Thermal Anneal/Oxidation System in pure nitrogen environment at 400 °C.

### 2.2 Characterization methods

The crystalline phase and quality of the ZnO films was analyzed by 2-theta and rocking curve scans with Siemens/Bruker D5000 X-ray Diffractometer (XRD). Since the size of the substrates were identical (1.5 cm × 1.5 cm) with similar film thicknesses, the intensity and full width at half maximum (FWHM) of the 2-theta scans could be used to compare the tendencies of the preferred orientations of the sputtered ZnO thin films. Assuming high purity 6 mm symmetry hexagonal ZnO thin film, the residual stress could then be estimated with the measured 2θ in the 2-theta scan in the following equation [12],

$$\sigma_{\text{ZnO}} = \frac{E_{\text{ZnO}} \Delta 2\theta}{(1 + v_{\text{ZnO}}) 2 \tan \theta_0},$$

where $\sigma_{\text{ZnO}}$ is the residual stress within the ZnO film, $E_{\text{ZnO}}$ and $v_{\text{ZnO}}$ are the Young’s modulus and Poisson ratio of the ZnO film respectively, $\theta_0=17.211$ is the Bragg angle under stress-free condition, and $\Delta 2\theta$ is the difference between the measured $2\theta$ and $2\theta_0$.

Surface morphology, grain size, and grain boundaries of the sputtered ZnO thin film were studied with scanning electron microscopy (SEM) (Carl Zeiss Ultra 55 SEM) to image both the surfaces and the cross-sections of the samples.

### 3 Results and discussions

#### 3.1 One-step and two-step depositions

To study the effects of the two-step deposition process on the growth of c-axis oriented ZnO polycrystalline structures, two deposition conditions (O1 and T2) were compared. The only difference between the two set of experiments was the addition of a 1 min pre-deposition step at 100 W prior to the 300 W main deposition step in T2. At the end of the pre-deposition step, the RF power level was ramped up from 100 W to 300 W in less than one second. Figure 1 shows the diffraction spectra of the ZnO films sputtered under these two deposition conditions on four different substrates, where the gray lines and the black lines are results of the one-step and two-step depositions, respectively. The intensities and FWHM values are listed in Tables 3 and 4. It should be noted that the only peak in

<table>
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<th>Table 2</th>
<th>Six designed ZnO sputtering conditions with 17 mtorr deposition pressure</th>
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<tr>
<td>Ar:O ratio</td>
<td>Pre-sputtering (RF Power/Time)</td>
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<tr>
<td>O1</td>
<td>100% Ar</td>
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<td>T2</td>
<td>100% Ar</td>
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<td>T3</td>
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<tr>
<td>T5</td>
<td>Ar:O = 11:2</td>
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<td>T6</td>
<td>100% Ar</td>
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each of the diffraction spectra is located around 34.42°, which originated from the (002) plane of the ZnO films. The spectra at 31.77° and 36.25°, representing (100) and (101) planes respectively, did not register observable signals. Thus, all the ZnO thin films deposited on four different substrates with two different methods show a good c-axis orientation. The spectral peaks located around 38° on Au/Ti/SiO₂/Si and Au/Ti/Si samples are the diffractions from the (111) plane in the underlying gold films.

It can be concluded from Fig. 1 and Tables 3 and 4 that two-step depositions did not enhance c-axis orientation in the ZnO films sputtered on Si and SiO₂/Si substrates. However, its effect was significant on the metal-coated surfaces. The intensities of the (002) peaks from the two-step deposited films on Au/Ti/Si or Au/Ti/SiO₂/Si are about 4 times higher than the corresponding ones from one-step deposition. The FWHM values show similar trends. This is clear evidence that two-step depositions result in an enhanced c-axis oriented ZnO films when sputtered onto Au/Ti/Si or Au/Ti/SiO₂/Si surfaces.

Another important observation is that the intensities of the (002) peaks from ZnO sputtered on Au/Ti/SiO₂/Si are one order of magnitude higher than those on Au/Ti/Si, and their FWHM are also narrower. This indicates that the layer of amorphous SiO₂ between the native silicon surface and the Au/Ti layer allowed significant enhancements in growing c-axis ZnO crystalline. It should be emphasized that this effect is true for both one-step and two-step deposition methods. A possible explanation is that the amorphous SiO₂ effectively masked the crystalline surface of the (100) silicon wafer, allowing the formation of native crystalline structures of the metals films deposited on top. The spectral peak intensities from the (111) planes of the Au films shown in Fig. 1 are consistent with this explanation. The intensities of the (111) peaks from Au on Au/Ti/SiO₂/Si substrate is 5 times higher than those from Au/Ti/Si.

3.2 Substrates

Three sets of deposition conditions, T3, T4, and T5, were designed to investigate substrate influences on film qualities. In all three sets, a two-step deposition method with one minute pre-deposition step was utilized. Figure 2a shows the diffraction spectra of the deposited ZnO thin films with 350 W (gray lines) and 400 W (black lines) RF power during the main deposition steps in T3 and T4, respectively. It is clear from Fig. 2a and the spectral intensity results in Table 3 that Au/Ti/SiO₂/Si surfaces offered the best possible ZnO films regardless of the deposition RF power levels. This is true even with the one-step deposition approach, as indicated in spectral intensity results for condition O1 in Table 3. Note also that the intensity and FWHM value of condition T3 has the highest value among the three different deposition conditions (Tables 2 and 3), indicating that the optimal deposition RF power for two-step deposition is 350 W.

To further investigate substrate dependency, a deposition condition, T5, which was less favorable for c-axis ZnO growth was performed. The Ar/O ratio was set to 11:2, resulting in an over-abundance of oxygen gas during sputtering. Figure 2b shows the diffraction spectra of the
ZnO thin films deposited under this condition with two-step deposition method. The deposited ZnO thin films on Si and SiO2/Si substrates do not show any preferred orientation in (002) plane, and the peaks at (100) and (101) planes exhibit compatible intensities with (002) plane in the diffraction spectra. In contrast, the ZnO thin films sputtered on Au/Ti surfaces showed substantial preference for c-axis orientation. Also, the Au/Ti/SiO2/Si substrates exhibit a stronger effect than Au/Ti/Si, which is consistent with other deposition conditions.

Figure 3a shows the rocking curves of the deposited ZnO thin films with T3 deposition condition. The peak rocking curve intensity of the ZnO sputtered on Au/Ti/SiO2/Si substrate is 5.2 times higher than that on Au/Ti/Si substrate, 31 times higher than that on Si substrate, and 50.5 times higher than that on SiO2/Si substrate. The FWHM values of the Au/Ti/SiO2/Si and Au/Ti/Si substrates are 4.2° and 7.4°, respectively, exceeding or matching the 7° from the high quality ZnO films reported in [13]. Figure 3b shows the rocking curves of the ZnO grown in the adverse condition T5 on Au/Ti/Si and Au/Ti/SiO2/Si substrates. Although both intensities are low in contrast to the best deposition practices, the FWHM of the ZnO films sputtered on Au/Ti/SiO2/Si substrate is still at 7.7°, which is still acceptable.

Figures 4 and 5 show the SEM of the surfaces and cross-sections of sputtered ZnO thin films on four different substrates under T3 deposition condition. Figures 4a and 5a are images of ZnO deposited on Si substrate, Figs. 4b and 5b are those of ZnO on SiO2/Si substrate, Figs. 4c and 5c are those on Au/Ti/Si substrate, and Figs. 4d and 5d are those on Au/Ti/SiO2/Si substrate. The layered substrates
are clearly shown in Fig. 5. Figures 4a, b, and c clearly indicate that the ZnO thin films are polycrystalline. Figures 5a, b, and c show the grain boundaries of the columnar structures within the films. It should be noted that the grain size of the polycrystalline ZnO on Si and SiO$_2$/Si substrates are smaller than those on Au/Ti/Si substrate. This is an evidence that Au coated substrates support larger grain growth and thus higher film qualities. Furthermore, Figures 5a, b, and c show that the directions of the polycrystalline grains are not necessarily uniform, resulting in spectral broadening and peak suppression of the (002) plane. The piezoelectric effects in these films would be compromised considerably [14].

Figures 4d and 5d are the SEM of the surfaces and cross-sections of the ZnO thin film sputtered on Au/Ti/SiO$_2$/Si substrate. The surface morphology of this film is different than those indicated in Figs. 4a, b, and c. On close examination, two types of ZnO crystalline structures can be identified in this thin film. Part of the film is polycrystalline, with grain size larger than those on Au/Ti/Si substrate. The grain size of the rest of the crystalline structures is substantially smaller. This morphology is visible on the cross-sectional view of this region (Fig. 5d). The c-axis orientation, and thus the piezoelectric effects, is dominated by the smaller crystalline structures, resulting in high quality thin films.
3.3 Pre-deposition duration

Deposition condition T6 differs from T3 only in the lengthened pre-deposition duration from 1 to 5 min, with all other parameters held the same. Figures 6a compared the diffraction spectra of the ZnO thin films with 1 min (gray line) and 5 min (black line) pre-deposition durations. The peak intensities and FWHM values are very similar, but the 2θ value increases from 34.08° to 34.12°, while the residual stress decreases slightly from –636.46 MPa to –562.17 MPa. The influence of the pre-deposition duration is more obvious in the rocking curves shown in Fig. 6b. The peak intensity of the deposited ZnO thin films with 5-min (black line) pre-deposition is 4.3 times higher than that with 1-min pre-deposition (gray line). Furthermore, the FWHM value was reduced from 4.2° to 2.21°. To investigate further, SEM images of the ZnO surface and its cross-section were taken, which are shown in Figs. 7a and b. Comparing Figs. 7a and 4d, it is obvious that the percentage of large polycrystalline ZnO grains is substantially lower with 5 min pre-deposition duration (T6). The cross-sectional SEM shown in Fig. 7b also shows that the c-axis of the deposited crystalline ZnO grains is very well aligned and the grain boundaries are not obvious. These observations offer the explanations why the film quality is higher as a result of better c-axis orientation with longer pre-deposition.

3.4 Postdeposition annealing

To prevent the problems of film cracking and bulking, as well as slow relaxation over time resulting in performance drifts, the necessary post-deposition annealing time was investigated. The annealing temperature was chosen to be 400 °C in 100% nitrogen ambient [8].

Figure 8 shows the stress relaxation curve, with the residual stresses of the ZnO thin films sputtered on Au/Ti/SiO₂/Si substrate with 5 min of pre-deposition. The residual stress reduces from –562.17 MPa to –152.60 MPa within 1 h, reaching –115.38 MPa after 8 h of annealing.

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![Fig. 6](image_url) XRD 2θ (a) and Rocking curve (b) scans of ZnO thin film growth on Au/Ti/SiO₂/Si substrate under 1 min. (gray lines) and 5 min. (dark lines) pre-deposition conditions

![Fig. 7](image_url) Scanning electron micrographs of the (a) surface and (b) cross-sections of the ZnO thin films deposited on Au/Ti/SiO₂/Si substrate under 5 min. pre-deposition conditions and the scale bar is 200 nm
This result indicates that 1 h annealing time should be sufficient to release a good portion of the residual stress due to film defects and dislocations. The remaining residual stress could originate from the thermal expansion coefficient mismatch between the substrates and the ZnO thin film. In particular, the 150-nm thick Au film has a high thermal expansion coefficient compared to other materials. This could cause chip bowing, and Eq. (1) would no longer apply [7]. Chip bowing could be minimized by etching part of the ZnO thin film.

Stress relaxation curves for ZnO on SiO₂/Si (dotted line), Si (dashed line), and Au/Ti/Si (dark line) substrates are also shown in Fig. 8. After 30 min of annealing, the residual stresses of the ZnO on SiO₂/Si, Si, and Au/Ti/Si substrates reduced to 70.71 MPa, 33.49 MPa, and -40.9 MPa, respectively. This implies that 30 min annealing is too long for SiO₂/Si and Si substrates, with the tensile stress caused by thermal expansion overcoming the compressive built-in stress of the ZnO thin film. Crack lines were observed on the ZnO thin film on Au/Ti/Si substrate afterward, as shown in the SEM in Fig. 9. It also implies that a layer of thermal oxide between the Au/Ti film and the silicon wafer could substantially alleviate the consequences of thermal expansion mismatches between different layers.

4 Conclusion

With six sets of carefully designed ZnO deposition conditions, the influences of the layered substrates and the two-step deposition process on the film quality were investigated and identified. The Au/Ti layer facilitated the growth of ZnO rich in c-axis oriented polycrystalline microstructures regardless of all other varying deposition parameters. A thermally grown amorphous SiO₂ layer provided an excellent surface for depositing high quality Au/Ti films by masking the crystalline surface of the silicon wafer. Therefore, the best ZnO thin films were obtained by sputtering on Au/Ti/SiO₂/Si surface, which was confirmed with XRD data and SEM images. By incorporating a two-step deposition method with a lower power pre-deposition step to create a fine seed layer on Au/Ti/SiO₂/Si substrate, the tendency of c-axis preferred oriented ZnO was enhanced substantially. Furthermore, it was demonstrated that a 5-min pre-deposition time allowed a better seed layer to form than the 1-min pre-deposition. Well oriented c-axis ZnO thin film with substantially smaller grain size was demonstrated. The annealing time needed to release the residual stress from defects and dislocations inside the ZnO films was investigated. A 1-h annealing at 400 °C in pure nitrogen ambient released most of the residual stresses cumulated in the ZnO films deposited on Au/Ti/SiO₂/Si substrate.

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