Nitrogen [N]-incorporated ZnO piezoelectric thin films and their application for ultra-small film bulk acoustic wave resonator device fabrication

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Nitrogen [N]-incorporated ZnO films with columnar grains of a preferred c-axis orientation were deposited on p-Si (100) wafers, using an RF magnetron sputter deposition technique. For the N incorporation into the ZnO films, an N2O gas was used as a doping source and also various process conditions such as N2O gas fraction and RF power were applied. Besides, some of the ZnO films were treated with the post annealing process. And then, the micro-structural characteristics of the N-incorporated ZnO films were investigated by a scanning electron microscope, an X-ray diffractometer, and an atomic force microscope techniques. Finally, employing the N-incorporated ZnO films, the solidly mounted resonator-type film bulk acoustic wave resonator devices were fabricated and their resonance characteristics were extracted. As a result, an excellent return loss (S11) of −63 dB was observed at ~0.6 GHz, better than ever reported.

I. INTRODUCTION

Zinc oxide (ZnO) is a very important material for the application of optoelectronics, lasing, and piezoelectricity devices such as actuators, sensors, filters, and resonators. Especially, the film bulk acoustic resonator (FBAR) devices based on the piezoelectric characteristics of the ZnO films have attracted a great attention as a promising novel filter technology mainly because they are very likely to be fully integrated with the conventional complementary metal oxide semiconductor and radio frequency integrated circuit fabrication technologies, expectedly allowing for the realization of a single-chip radio or a transceiver in the future. In order to achieve a good performance of the FBAR devices by minimizing their insertion losses, it seems important to develop the high quality piezoelectric ZnO films that have the c-axis oriented textures, extremely smooth surfaces, sharp interfaces, and higher electrical resistivity.2

On the other hand, the intrinsic ZnO films grown hydrothermally have been usually observed to be a natively n-type semiconductor with less than $10^{14}$ cm$^{-3}$ of the compensated electron concentration.3 Thus, the compensatory-doped ZnO piezoelectric films are expected to have higher resistivity, leading to the better performance of the FBAR devices.

In this work, the compensatory nitrogen [N] doping has been implemented onto the ZnO films in an RF magnetron sputtering system using N2O gas as a doping source in an effort to further improve the resonance characteristics of the FBAR devices. Interestingly, it was observed that the N doping can change the electrical resistivity and the microstructures of the ZnO films. Although the microstructures of the ZnO piezoelectric films were reported to profoundly affect the FBAR device performance, relatively little is known about the study on the micro-structures and related physical characteristics of the compensatory-doped ZnO films particularly deposited in an RF magnetron sputtering system. From this standpoint, an analysis of microstructures needs to be done for more precise control of the N-doped ZnO films, contributing to enhance the device performance. The effects of the N-incorporation into the ZnO films due to the compensatory nitrogen [N] doping were inspected in detail and compared to the intrinsic ZnO films deposited in an O2/Ar gas mixture ambient normally used for the sputter-deposition of the ZnO films of the FBAR devices. Also, various N-incorporated ZnO (ZnO:N) thin films were deposited under various process conditions and some of them were thermally treated after deposited. Then, the investigation was made in order to understand how the variation of process conditions or the post-annealing treatments may affect the structural properties of the ZnO films. Finally, we have fabricated the solidly mounted resonator (SMR)-type FBAR devices by applying the compensatory N-doped ZnO thin films along with various kinds of the post thermal annealing treatments. The resonance characteristics of the fabricated FBAR devices were evaluated in terms of the return loss (S11).

II. EXPERIMENTS

The experiments were carried out largely in three main parts. The first part is mainly for comparison of the microscopic structural properties of the non-doped (intrinsic) ZnO thin films and the intentionally doped (i.e., N-incorporated) ZnO thin films. All ZnO films were deposited in an RF magnetron sputtering system using ZnO targets and Si (100) wafers (4-inch, p-type) as a substrate. The deposition details of the ZnO films are summarized in a section of Table I. Based on the experimental findings, the formation process of the ZnO films was optimized and selectively employed for the fabrication of various kinds of the ZnO films. As a result, for the first experiment, the RF power condition was fixed at 300 W, and the gas mixture ratios, i.e., [N2O/(N2O + Ar)] and [110] American Institute of Physics
[O₂/(O₂ + Ar)], were tuned both in 40%. After the formation of the ZnO films, the scanning electron microscope (SEM), x-ray diffractometer (XRD), and atomic force microscope (AFM) techniques were used for investigating the structural properties of the ZnO films such as the crystal quality and surface morphology, as described in Secs. III A 1 and III A 2.

The experiments in the second part were conducted to find out an optimum process condition by examining the physical properties of the N-incorporated ZnO films deposited under various process conditions along with the post-annealing treatments. Both partial N₂O gas ratios, i.e., [N₂O/(N₂O + Ar)] and deposition powers were controlled as two major deposition variables, as shown in B section of Table I. On the other hand, the N-incorporated ZnO films deposited at both the RF power of 300 W and the partial N₂O gas ratio of 40% were divided into the three samples (N1–N3) to carry out various thermal annealing treatments, as shown in C section of Table I. And then, the SEM, XRD, and AFM analyses were performed and their results were discussed in Secs. III A 3–III A 5.

In the final part, the SMR-type FBAR devices employing the N-incorporated ZnO films were fabricated on the basis of the property analysis of the N-incorporated ZnO thin films, and the FBAR fabrication sequence is as follows. First, the multi-layered Bragg reflector (BR) blocks were formed by alternately depositing both SiO₂ (low acoustic impedance material) and W (high acoustic impedance material) thin-film layers on a Si wafer where both the SiO₂ and W layers are 0.6 μm-thick. Then, the 1.0 μm-thick aluminum (Al) bottom electrodes were formed on top of the BR blocks. This was followed by the deposition of the ZnO piezoelectric thin films in a mixture ambient of N₂O and Ar gases while setting both the RF power at 300 W and the partial N₂O gas ratio in 40%. Immediately after the ZnO film deposition, the wafers were divided into five samples (S1–S5) to carry out various thermal annealing treatments, as shown in Table II. Then, the deposition and patterning of the 0.2 μm-thick Al top electrodes on top of the annealed or non-annealed ZnO films completed the FBAR device fabrication. Finally, the return loss (S₁₁) characteristics, as analyzed in Sec. III B, were measured by using an S-parameter measurement system including a probe station and Agilent E8361A PNA network analyzer.

### TABLE I. Process conditions of the ZnO films

<table>
<thead>
<tr>
<th>Variables</th>
<th>Pre-sputtering</th>
<th>Base pressure</th>
<th>Working pressure</th>
<th>Working gas</th>
<th>Substrate</th>
<th>Temperature</th>
<th>Rotation speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Deposition conditions</td>
<td>15 min</td>
<td>5 × 10⁻⁶ Torr</td>
<td>20 mTorr</td>
<td>N₂O/Ar mixture or O₂/Ar mixture</td>
<td>Room temperature</td>
<td>8 rpm</td>
<td></td>
</tr>
<tr>
<td>RF power</td>
<td>80 W, 120 W, 180 W, 240 W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### TABLE II. Various annealing conditions of the FBAR devices.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Annealing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Non-annealed</td>
</tr>
<tr>
<td>S2</td>
<td>Annealed at 200°C/10 min (in an O₂ gas ambient)</td>
</tr>
<tr>
<td>S3</td>
<td>Annealed at 300°C/10 min (in an O₂ gas ambient)</td>
</tr>
<tr>
<td>S4</td>
<td>Annealed at 400°C/10 min (in an O₂ gas ambient)</td>
</tr>
<tr>
<td>S5</td>
<td>Annealed at 500°C/10 min (in an O₂ gas ambient)</td>
</tr>
</tbody>
</table>

### III. RESULTS AND DISCUSSION

#### A. Effects of process conditions on the structural and micro-structural properties of the intrinsic ZnO thin films

Nitrogen [N] atom was reported as one of the elements that can effectively compensate the native n-type conductivity characteristics of the ZnO films. This is because, among the group V impurities, the N atom has the smallest ionization energy and also it does not form the N₂Zn antisite. Various kinds of the N sources can exist in various compound forms such as N₂, NO, N₂O, NH₃, Zn₃N₂, CH₃COONH₄, and NH₂NO₃, and thus one of them can be selectively employed corresponding to the film growth technologies.

The N₂O gas seems to have some advantages as follows. It has a relatively lower dissociation energy (N-N: 5.16 eV, N-O: 6.37 eV) as well as a lower ionization potential (N₂O: 12.9 eV) as compared to the N₂ gas having the dissociation energy (N-N: 9.76 eV) and ionization potential (N₂: 15.65 eV), respectively. This means that the N atoms can be more easily dissociated from N₂O than from N₂, and moreover, the N₂O gas is not poisonous. In this reason, N₂O gas was selected as a doping source for the N-incorporation that can lead to a high resistivity of the ZnO films fabricated in this work. As a consequence of the four-point probe measurements, the electrical resistivities of the N-incorporated ZnO films and the intrinsic ZnO films were obtained as 4.24 × 10⁴ Ωcm and 3.92 × 10³ Ωcm, respectively. Thus, the N-incorporated ZnO films were found to have the higher resistivity by about one order of magnitude than the intrinsic ZnO films, implying the presence of the compensatory doping effect.

Fig. 1 shows the XRD θ-2θ scan results and SEM cross-sectional view images of both intrinsic ZnO films and N-incorporated ZnO films deposited using the (O₂/Ar) and (N₂O/Ar) gas mixture, respectively. It is noted that both ZnO films were deposited at the same gas mixture ratio, i.e., [N₂O/(N₂O + Ar)] or [O₂/(O₂ + Ar)] tuned in 40% and both at the same RF power of 300 W. It was found that only one strong (002) peak appeared in the intrinsic ZnO films while the relatively weak (002) peak was found together with other weaker (101) and (100) peaks in the N-incorporated ZnO films. This means that the N-incorporated ZnO films still exhibit a trend of the c-axis oriented columnar-type crystal growth trend, but its growth orientation preference towards the c-axis orientation is relatively weakened as compared to the intrinsic ZnO film growth.
Fig. 2 illustrates both the XRD rocking curves and the SEM top-view images of the intrinsic ZnO films and the N-incorporated ZnO films. The full width at half maximum (FWHM) values of the (002) diffraction peaks are 11.59° and 13.95°, respectively, in the intrinsic ZnO film and N-incorporated ZnO film. The FWHM value may be influenced by many factors such as grain size, stress distribution, and crystal imperfection and also can be used as an indicator of the film crystal quality. In this work, the N-incorporated ZnO films have shown smaller grains in size with relatively larger FWHM values as compared to the intrinsic ZnO films. Thus, the c-axis preferential orientation of the ZnO films seems to be degraded by the incorporation of the N atoms into the ZnO films. This result is explained by the fact that the substitutional built-ins of the N atoms onto the zinc lattice sites may induce a possible internal stress and this stress, in turn, may create some lattice distortions, thus finally having a certain impact on the microstructures or crystal properties of the ZnO films deposited.
2. Effects of N-incorporation on the surface morphology of the ZnO films

Fig. 3 shows the AFM analysis performed to estimate the surface morphology and roughness of the ZnO films. The surface RMS roughness values of the intrinsic ZnO film and N-incorporated ZnO film were 16.14 nm and 5.53 nm, respectively. This indicates that the surface of the N-incorporated ZnO films is obviously much smoother than that of the intrinsic ZnO film mainly due to the N-incorporation into the ZnO films. This is speculated to be related to the crystallographic structures and growth characteristics of the ZnO films. The ZnO has a wurtzite structure, with \(0001\) planes being Zn-terminated and \(000\bar{1}\) planes being O-terminated. These two crystallographic planes have opposite polarity, hence having different surface relaxation energies. Thus, the improvement of the surface morphology of the ZnO films caused by the incorporation of the N atoms into the ZnO films can be possibly attributed to the low surface energy.

3. Effects of N2O gas ratio on the microstructures of the deposited ZnO films

Even though the N atoms can be easily dissociated from N2O gas, the solid solubility of the N atoms within the ZnO films is very low. Thus, it seems necessary to find out an optimum partial N2O gas ratio such that the N atoms can be incorporated into the ZnO films, eventually having an effect on the ZnO film properties. From this point of view, the effects of the N2O gas ratio, \([\text{N}_2\text{O}]/(\text{N}_2\text{O} + \text{Ar})\), on the microstructures (grain sizes or surface morphologies) of the ZnO films were investigated. Several kinds of the deposited ZnO films were prepared for various N2O gas ratios (0%–60%) and all at the same RF deposition power of 120 W.

Fig. 4 exhibits the SEM top-view images of the N-incorporated ZnO films deposited for various N2O gas ratios. N2O/(N2O + Ar) = (a) 0%, (b) 30%, (c) 40%, (d) 60%.

no significant differences in their surface morphologies were observed between the ZnO films of above 40% N2O gas ratios, as shown in (c) and (d). Thus, in this work, the optimal N2O gas ratio could be around 40%.

4. Effects of RF power on the microstructures of the ZnO:N films

RF power is also one of the primary process parameters that determine the microstructures particularly of the sputter-deposited ZnO films. The deposition of the ZnO films was performed at the fixed N2O gas ratio of 40% for several different RF powers (80 W, 120 W, 180 W, and 240 W). It is noted that the N2O gas ratio of 40% was selected in this work with an expectation that the N atoms can be incorporated into the ZnO films much enough to have an appreciable impact on the structural properties of the ZnO thin films.

Figs. 5 and 6 show the SEM images, respectively, of the surface morphologies and cross-sectional views of the
N-incorporated ZnO films deposited at various deposition RF powers. With the relatively lower deposition power (80 W) applied, very small and uniform size grains were found to grow in the ZnO films. With gradual increase in the deposition power, the relatively larger and less uniform size grains were grown, the growth rates of the ZnO films increased, and also the c-axis preferred orientation characteristics were gradually enhanced. It is speculated that during the ZnO film deposition, the higher RF power seems to increase the substrate temperature and this, in turn, may have an influence on the initial stages of the grain nucleation, eventually determining the overall grain growth mechanism.9

5. Effects of post-annealing treatment on the microstructures of the ZnO:N films

In general, the annealing treatments have been used for improving the film quality, thereby leading to the performance improvement of the FBAR devices.10,11 In this work, the effects of the post-annealing treatments on the microstructures of the N-incorporated ZnO films were investigated for the first time.

Fig. 7 presents the XRD θ-2θ scan results and rocking curves of the N-incorporated ZnO thin films, either non-annealed or with the post-annealing treatments (300°C–500°C). The c-axis preferred orientations along with other weak diffraction peaks appeared in the samples (N1, N2, N3) and their FWHM values were 13.95°, 17.66°, 16.66°, respectively. While all samples show little difference in the c-axis orientation preference regardless of the annealing process (300°C–500°C), the FWHM value of the non-annealed sample (N1) seems much smaller as compared to those of the annealed samples (N2, N3).

From the AFM analysis, the surface RMS roughness values of three samples (N1–N3) were 5.529, 5.313, and 5.529.
6.793 nm, respectively. There is no significant difference in the roughness between the N1 and N2 samples, and the surface RMS roughness of the N3 sample is relatively higher.

On the other hand, the electric resistivities of the post-annealed samples were found to be $1.71 \times 10^4 \ \Omega \cdot cm$ (300°C), $1.95 \times 10^4 \ \Omega \cdot cm$ (400°C), and $6.25 \times 10^2 \ \Omega \cdot cm$ (500°C), respectively. Compared to the electric resistivity of the non-annealed ZnO film, the N3 sample alone shows a considerably lower value while there is little significant difference in the case of other samples (N1, N2).

B. Fabrication of FBAR devices employing the ZnO:N films

The structures of conventional FBAR device are usually made up of a thin piezoelectric film layer sandwiched between top and bottom electrodes where an acoustic wave resonance occurs when an RF signal is applied across the electrodes. Also, the FBAR devices have a BR block that can act as a mirror plane to prevent a possible energy loss into the substrate from the resonating piezoelectric part. In the past, considerable researches have been performed into the substrate from the resonating piezoelectric part. In the past, considerable researches have been performed to realize even higher quality ZnO films in an effort to improve the FBAR device characteristics. Traditionally, the O$_2$/Ar gas mixture has been employed as a reactive gas for the ZnO film deposition, followed by thermal annealing treatments for further enhancement of the resonance performance. It has been also reported that the thermal post-annealing process at an optimum temperature could further improve the resonance characteristics of the FBAR devices based on the multi-layered Bragg reflectors due to the effective elimination of any physical imperfections inside the sandwiched device structures.

In this work, we for the first time report the study on the FBAR devices operating at ~0.6 GHz that were fabricated employing the N-incorporated ZnO piezoelectric thin films deposited under more systematically optimized process conditions, along with various post-annealing treatments.

Fig. 8 shows the plots of the return loss characteristics ($S_{11}$) (versus the resonance frequency) extracted from the five samples (S1–S5), and also their peak return loss values were summarized in Table III. The annealed FBAR devices on the samples (S2–S5) have shown much better resonance characteristics as compared to the non-annealed devices on the S1 sample. It is interesting that the $S_{11}$ degradation was observed particularly when the annealing temperature increased from 300°C to 500°C, implying that there is an optimum annealing condition. Moreover, the measurements show that in the sample S3, an excellent return loss ($S_{11}$) value of ~63 dB could be achieved at ~0.6 GHz, even better than ever reported in this FBAR device technology regime.

Judging from both the previous analyses on the structural properties of the N-incorporated ZnO films and the return loss ($S_{11}$) measurements of the fabricated FBAR devices, the N-incorporation into the ZnO films seems to slightly reduce the crystal quality of the ZnO piezoelectric films. Nevertheless, with the introduction of the N atoms into the ZnO films, the ZnO piezoelectric films can advantageously have the extraordinarily smooth surfaces as well as the relatively higher resistivity characteristics. It has been reported that the rough surfaces of the ZnO piezoelectric films in the acoustic wave devices including the FBAR devices could enlarge the insertion loss of the devices. Furthermore, the surface morphology may be able to highly influence the adhesion property of the interfaces between the ZnO films and top electrodes formed right onto them in addition to the quality of the top electrodes, thus having a significant impact on the resonance characteristics. In this reason, it is very critical to form the ZnO piezoelectric thin films of very smooth surfaces for the better performance of the FBAR devices.

On the other hand, the N-incorporated ZnO thin films, treated thermally at the various temperatures, were slightly degraded in the crystal quality and have shown very little change in the surface morphology, but the FBAR devices have still shown the excellent return loss ($S_{11}$) characteristics. It is speculated that the annealing treatments at the optimal temperature, despite of a slight degradation in the crystal quality of the N-incorporated ZnO films, could definitely improve the performance of the Bragg reflector, generally enhance the adhesion between the film layers, and especially intensify the adhesion between the N-incorporated ZnO films with the very smooth surfaces and the top electrodes, thus overall creating a synergistic improvement of the FBAR device characteristics.

### IV. CONCLUSION

The nitrogen [N]-incorporated ZnO films with the preferred c-axis growth orientations were prepared on the p-Si (100) wafers in an RF magnetron sputtering system. N$_2$O gas was employed as an N doping source and various process samples (S1–S5).

### Table III. Peak return loss values of the fabricated FBAR devices on the samples (S1–S5).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak return losses, $S_{11}$ (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (non-annealed)</td>
<td>-14.24</td>
</tr>
<tr>
<td>S2 (annealed at 200°C/10 min)</td>
<td>-49.67</td>
</tr>
<tr>
<td>S3 (annealed at 300°C/10 min)</td>
<td>-62.83</td>
</tr>
<tr>
<td>S4 (annealed at 400°C/10 min)</td>
<td>-58.74</td>
</tr>
<tr>
<td>S5 (annealed at 500°C/10 min)</td>
<td>-43.02</td>
</tr>
</tbody>
</table>

FIG. 8. Return loss characteristics ($S_{11}$) versus frequency for the fabricated samples (S1–S5).
conditions such as N$_2$O gas fractions and RF powers were applied. Additionally, some of the fabricated samples were treated with the post-annealing process. Due to the incorporation of the N atoms into the ZnO films, much significantly smoother, flatter, and more uniform ZnO film surfaces could be obtained, whereas the ZnO film crystal quality is slightly degraded. And also, the effects of the annealing treatments on the N-incorporated ZnO films seem very small in the microstructure changes of the ZnO:N films.

On the other hand, we for the first time report a new approach to fabricate the FBAR devices employing the ZnO:N films particularly sputter-deposited in a mixture of N$_2$O and Ar gases as the reactive and sputtering gases, respectively. In addition, various post thermal-annealing treatments and their effects on the N-incorporated ZnO films were studied. As a result, the FBAR devices employing the N-incorporated ZnO films annealed at 300 °C/10 min showed an excellent resonance characteristic in terms of the return loss ($S_{11}$) of 62.83 dB at ~0.6 GHz. To our knowledge, it is the most outstanding result, ever reported in this FBAR device technology regime. This proposed approach seems very promising and useful for the future FBAR devices and their applications.

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