Combinatorial approach to MgHf co-doped AlN thin films for Vibrational Energy Harvesters

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Abstract. In this report, we studied MgHf co-doped AlN ((Mg,Hf)\(_x\)Al\(_{1-x}\)N) aiming for developing an AlN-based dielectric material with the large piezoelectric coefficient. To rapidly screen the wide range of composition, we applied combinatorial film growth approach. To get continuous composition gradient on a single substrate, films were deposited on Si (100) substrates by sputtering AlN and Mg-Hf targets simultaneously. Crystal structure was investigated by X-ray diffractometer equipped with a two-dimensional detector (2D-XRD). Composition was determined by Energy Dispersive Spectroscopy (EDS). These studies revealed that we successfully covered the widest ever composition range of 0 < \(x\) < 0.24 for this material. In addition, these studies found that we succeeded in realizing largest ever c-axis expansion of 2.7\% at \(x = 0.24\), which will lead to the highest enhancement in the piezoelectric coefficient. The results of this study opened the way for high-throughput development of the dielectric materials.

1. Introduction

Recently due to the restriction of lead in industry, lead-free materials have received considerable interest from many scientists for applications such as vibrational energy harvesters (VEHs) [1]-[4]. Among the lead-free piezoelectric materials that have been studied, c-axis oriented AlN film is a good candidate for the piezoelectric thin film for VEHs because of its high breakdown voltage [4] and high output power density [1]. However compared with the traditional lead zirconate titanate (PZT), piezoelectric coefficient of the AlN \(d_{31} \sim 5.5\) pC/N for AlN and \(\sim 100\) pC/N for PZT[5]) is very low [1], [4]-[10]. Therefore, one of the important topics is to improve AlN piezoelectricity. The most effective approach developed so far is modifying crystal structure of AlN using substitution of Al\(^{3+}\) site by other elements.

Among the systems studied so far, MgHf co-doped AlN ((Mg,Hf)\(_x\)Al\(_{1-x}\)N) showed the highest increase rate of \(d_{31}\) per dopant concentration (at\%). For example, Y. Iwazaki \textit{et al.} reported MgHf doping and \(d_{31}\) of AlN showed increase rate of 11.5\% [9]. This rate is the largest so far. However, in the previous study of (Mg,Hf)\(_x\)Al\(_{1-x}\)N, dopant concentration was limiter only to 13\% although the piezoelectric coefficient tends to increase more at higher concentration of dopants. Moreover, the important crystal characteristics including lattice constant, crystal orientation \textit{et al.} were not reported, though these parameters can be dominant on the \(d_{31}\).

In this study, to cover a wider range of the dopant concentration and systematically investigate the effect of the dopant concentration on the lattice expansion, combinatorial approach was employed. The combinatorial approach is a high-throughput material investigation method preparing films with various
composition on a single substrate. Moreover, the method enables us to precisely tune the concentration of dopants.

2. Experimental

AlN targets and Mg-Hf targets (Mg target with pieces of Hf on top) were sputtered simultaneously to grow films on Si (100) substrates. Number of Hf piece was adjusted in order to get Mg: Hf ~ 1:1. Figure 1 shows an illustration of the sputtering set up. A substrate holder and the targets were arranging to obtain composition gradient. Plasma gases used for sputtering were Ar and N₂. The latter was used to compensate the nitrogen deficiency in thin films. On the other hand, at a certain sputtering pressure, the presence of N₂ will reduce probability of collision between sputtered particles with a heavy atom of Ar. Hence, sputtered particle could reach to the substrate with higher energy, which assist the formation of higher crystallinity films [11]. Thin films were deposited at 600°C to get high crystallinity [4]. Other sputtering parameters were shown in Table 1.

| Table 1. Deposition conditions |
|--------------------------------|
| **Substrate temperature**     | 600°C |
| **RF power**                  |       |
| AlN gun                       | 140 W |
| MgHf gun                      | 100 W |
| **Accelerated voltage**       |       |
| AlN gun                       | 1200 V|
| MgHf gun                      | 1000 V|
| **Beam current**              |       |
| AlN gun                       | 38 mA |
| MgHf gun                      | 25 mA |
| **Sputtering pressure**       | 3.8 - 4 mTorr |
| **Film thickness**            | ~ 1 µm |
| **Ar gas flow rate**          | 15 sccm|
| **N₂ gas flow rate**          | 15 sccm|
| **Deposition time**           | 2 h    |

Prior to each thin film deposition, Si substrates were cleaned by standard cleaning processes of Radio Corporation of America (RCA1 and RCA2). Base pressure of the sputtering chamber was keep at less than 1 × 10⁻⁷ Torr. The AlN-target was pre-sputtered before each deposition for 20 minutes in Ar and then for 10 minutes in the mixture of Ar and N₂. Thicknesses of the films were controlled by sputtering time and measured by a surface profiler. The composition was confirmed by using the EDX spectroscopy. An atomic force microscopy (AFM, Nikon TE2000-U) was used to examine thin film surface roughness. X-ray diffractometer equipped with a two dimensional detector (2D-XRD) was employed for a measurement of crystallinity. Diameter of the focused X-ray beam was fixed at 1 mm.

3. Results and discussions

Figure 2 shows a typical picture of the film surface prepared by the combinatorial approach. Lateral color change indicates change in the thickness ratio of AlN to MgHf, which corresponds to dopant concentration. For the 2 cm × 2 cm sample, typical composition difference is 2.8 at.%. Focused X-ray
beam with spot diameter of 1 mm allowed for measurement of more than 15 points along the composition gradient.

XRD and EDS measurements confirmed that we succeeded in making solid solution of \((\text{Mg},\text{Hf})_x\text{Al}_{1-x}\)N at the highest concentration of dopant ever. Figure 3a shows a typical 2D-XRD pattern of a \((\text{Mg},\text{Hf})_{0.09}\text{Al}_{0.91}\)N film. Except a diffraction peak from Si substrate, only a peak from (0002) and (0004) plane of AlN were observed. Because we did not observe neither Mg nor Hf peaks, the pattern indicated that (Mg,Hf) dissolved in the AlN lattice. The solid solution was also indicated by the continuous peak shift from the (0002) peak of the pure AlN film [9], [10]. The integrated 2θ-θ patterns obtained from 2D-XRD patterns for different compositions of \((\text{Mg},\text{Hf})_x\text{Al}_{1-x}\)N thin films were shown in figure 3b. The continuous peak shift in the 2θ position of the (0002) peak indicated that c-axis lattice constant of the AlN was gradually expanded with increasing the dopant concentration.

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{1}{c^2}
\]

where, \(h\), \(k\) and \(l\) are Miller indices, \(a\) and \(c\) are lattice constants, \(d\) is inter-planar distance for \((hkl)\) plane (here is (002)). It clearly indicated that c-axis expanded with increase in the (Mg,Hf) concentration. Note that there is difference between the reference value and experimental value for \(x = 0\), which can be attributed to nitrogen deficiency.

The effect of the MgHf dopants on the surface morphologies of \((\text{Mg},\text{Hf})_x\text{Al}_{1-x}\)N films was investigated by atomic force microscopy (AFM). The results were shown in figure 5. AFM observation shows that root mean square (RMS) roughness of the thin films increase dramatically from 1.1 nm to 9.0 nm with increase in the dopant concentration \(x\) from 0 to 24.3 at%.
4. Conclusion

In summary, we successfully deposited \((\text{Mg,Hf})_x\text{Al}_{1-x}\text{N}\) films with composition gradient covering the widest range of composition \((0 < x < 0.24)\) so far reported. For these films the c-lattice of AlN was expanded almost linearly with the composition, and we obtained c-axis expansion of 2.7% at \(x = 0.24\), which is the largest value for this system. We believe future study will find the largest piezoelectric coefficient for \((\text{Mg,Hf})_x\text{Al}_{1-x}\text{N}\) among the AlN-based materials due to the largest c-axis expansion, prove the importance of this material for the vibrational energy harvesters.

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