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Mg and Ti codoping effect on the piezoelectric response of aluminum nitride thin films

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ABSTRACT

Enhancement of the piezoelectric response (d_{33}) of aluminum nitride (AlN) was attempted by incorporating Mg and/or Ti into AlN. Addition of either Mg or Ti as a single dopant was unable to effectively increase the d_{33} of AlN. However, the d_{33} could be augmented when both Mg and Ti were codoped into AlN. The optimum d_{33} (9.1 pC/N) was observed when Mg to Ti ratio was 1.3 and the (Mg + Ti) concentration was approximately 18 at.%. In this study, effect of Mg and Ti co-dopants on the d_{33} of thin films was elucidated from changes in crystallinity and chemical surface state.

Aluminum nitride (AlN) thin film is among the most intensively investigated thin films and its most attractive features over the other widely-used piezoelectric thin films such as lead-zirconate titanate (PZT) or ZnO is the high Curie temperature, which give a promise for high temperature applications [1]. AlN is also a relatively environmentally-benign material and has compatibility with the CMOS technology [2], which has widen the use of AlN for various electronic applications. Up to this day, AlN has been extensively utilized for BAW resonator in wireless telecommunication device [3]. One of the major drawbacks in AlN utilization is the low piezoelectric response. As the market for such devices continue to grow and to anticipate the exploitation of AlN for wider applications, improving the piezoelectric performance of AlN has been of interest for many researchers in this field.

Piezoelectricity can be generated when the non-centrosymmetric wurzite structure AlN receive a mechanical stress (direct piezoelectric effect) [4]. The piezoelectric response of a thin film can be characterized by a piezoelectric coefficient or constant (in this study: d_{33}). AlN generated better d_{33} when the AlN thin film is a highly *c*-oriented one [5]. Hence, one of the keys in improving the piezoelectric property of AlN is governing their growth in *c*- direction. Another effective method to promote higher d_{33} is by doping with other metal [6–8] and the most dramatic enhancement so far was obtained by addition of 40 at.% Sc [6]. However, the expensive cost of Sc that could potentially limit the wider applications of $Al_xSc_{1-x}N$, has inspired efforts for finding new dopant to replace Sc.

As a substitute for Sc, Yokoyama et al. reported that addition of Mg—Zr into AlN resulted in d_{33} that was three times greater than non-doped AlN [9]. The proposal to use MgZr co-dopants was later reinforced by Iwazaki et al. that has run a first-principle calculation to estimate the piezoelectric response of several other Mg-based codopants for AlN. Among the calculated Mg-based-codopants, the addition of MgTi is predicted to give a comparable piezoelectric response with that of ScAlN [10]. Furthermore, the utilization of low cost material such as Mg and Ti will be beneficial for practical applications. The use of Mg as a single dopant for AlN has been reported recently, where addition of low concentration of Mg could slightly improve the d_{33} [11]. However, there has not been any experimental report regarding the effect of Mg—Ti addition into AlN on the d_{33}. Given the promising prospect of Mg—Ti dopant as suggested in [10], the effect of Mg—Ti addition into AlN thin film is investigated in this study. Since having a highly c-oriented thin film is also an important factor in generating high piezoelectric response, the presence of (002) peak as the preferred orientation for the wurtzite structure was also examined. The preliminary results of this study have been previously reported in [12] and detail study on the effect of Mg and Ti addition on the piezoelectric response as well as the corresponding crystallinity and chemical surface state were conducted and the results are reported herein.

The thin film was fabricated via reactive sputtering by utilizing a radio frequency (r.f.) sputtering system that is equipped with triple targets, namely Al (99.999%, Raremetalic, Japan), Mg (99.99%, Raremetalic, Japan) and Ti (99.99%, Raremetalic, Japan). The concentration of dopants were adjusted by controlling the output power of the target during sputtering process. The $(Mg,Ti)_xAl_{1-x}N$ thin films were directly deposited on the surface of Si (100) wafer. Before the sputtering process, the sputtering chamber was evacuated to a pressure of $<3 \times 10^{-5}$ Pa.

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The deposition process was conducted at substrate temperature of 400 °C, the deposition pressure of 0.35 Pa and N_2 concentration of 50 vol%.

The concentration of dopants in the thin film was determined by an energy dispersive x-ray spectroscopy (Horiba, Japan). The (002) crystal phase of the obtained films were evaluated by subjecting each sample to XRD measurement using an x-ray diffractometer (RINT-TTR III, Rigaku, Japan). The interface of the thin film was studied using FE-SEM (JSM-7001F, JEOL, Japan). The x-ray photoelectron spectroscopy (XPS) measurements were performed using KRATOS Axis 165 with monochromatic Al Kα after subjected the thin film to 15 min of etching. The C*1s* line of 284.6 eV was used as reference to calibrate the binding energy. The piezoelectric response (d_{33}) was investigated by applying a low frequency force (0.25 N at 110 Hz) to the fabricated thin film using a Piezometer system (Piezotest PM300, UK).

Initially, each of Mg and Ti was introduced into AlN as a single dopant and the corresponding piezoelectric response (d_{33}) was examined. As shown in Fig.1(a), addition of Mg at low concentration (approximately 2.5 at.%) could slightly increase the d_{33}, while further addition of Mg led to lower d_{33} [11]. Fig. 1(b) reveals that incremental addition of Mg as single dopant resulted in the shift of (002) peaks towards lower degree which indicates an increase in the length of *c*-axis of the wurtzite structure with increasing Mg addition as a result of greater ionic radius of Mg^{2+} than Al^{3+} [13]. Incorporating Mg into AlN also led to a decreases in the intensity of (002) peak, which suggest that the amount of wurtzite structure in (002) phase decreases with increasing Mg concentration. Also, addition of Mg in large amount promotes the formation of additional (unknown) compound (indicated by * in Fig. 1(b)). It is evident that doping Mg into AlN affected the crystallinity of the resulting thin films.

Similar with Mg, the use of Ti as a single dopant was also unable to increase the d_{33} of AlN, even a small addition of Ti (2.8 at.%) led to lower d_{33} (Fig. 1(c)). The XRD pattern for Ti-AlN shows that addition of Ti also caused a shift of (002) peak towards lower degree, which suggests an expansion of *c*-axis with increasing Ti content (Fig. 1(d)), due to the greater ionic radius of either Ti^{4+} or Ti^{3+} than Al^{3+} [13,14]. Aside from that, addition of Ti has also influenced the crystallinity of the resulting thin film as suggested by the decrease in diffraction intensity and the appearance of new phase in the pattern. The intensity of (002) peak was found to decrease with increasing Ti content, which indicate a decrease in the amount of wurtzite structure with increasing Ti concentration. Furthermore, higher Ti addition (>17 at.%) also lead to the formation of additional (unknown) compound, as indicated by ♦ in Fig. 1(d).

The XRD results have confirmed that addition of either Mg or Ti deteriorates the crystallinity of the resulting thin film, as indicated by a decrease in the amount of wurtzite structure with increasing dopant (either Mg or Ti) concentration and the presence of additional compound. The degradation in crystallinity of the resulting thin film is suspected to contribute in generating lower d_{33}.

When Mg and Ti are simultaneously incorporated into AlN, a different result was observed. As can be seen in Fig. 2(a), the d_{33} could be enhanced up to 9.1 pC/N when the ratio of Mg to Ti is set to 1.3. Fig. 2 (b) shows d_{33} as a function of dopants (MgTi) concentration in the thin film with Mg to Ti ratio is set to 1.3 and 1.0. It can be seen that the optimum d_{33} can be achieved when the total dopants (Mg + Ti) concentration is approximately 18–19 at. % for both dopant (Mg/Ti) ratio of 1.0 and 1.3. The morphology of the fabricated MgTi-doped-AlN (Mg/Ti = 1.3 & Mg + Ti = 18 at.%) thin film was characterized by cross-section SEM, where it can be seen that the $(MgTi)_xAl_{1-x}N$ was grown on the Si (100) substrate with columnar structure and the thickness was observed to be about 700 nm (Fig. 3(a)).

In order to address why incorporating 18 at.% MgTi into AlN could enhanced d_{33}, the effect of MgTi addition into AlN was firstly investigated by confirming the crystal structure of the obtained $(MgTi)_xAl_{1-x}N$ thin films. Since the concentration dependence trend for thin films with Mg/Ti = 1 and Mg/Ti = 1.3 is similar, thin films with Mg/Ti = 1 are chosen here as the representative to explain the effect of MgTi codoping into AlN on the d_{33}. As shown in Fig. 3(b), addition of MgTi shift the (002) peaks towards lower degree, which can be inferred as an increase in the length of *c*-axis of the wurtzite structure with increasing MgTi content, due to the substitution of Al with Mg and Ti that have greater ionic radii than Al [13,14]. An expansion of

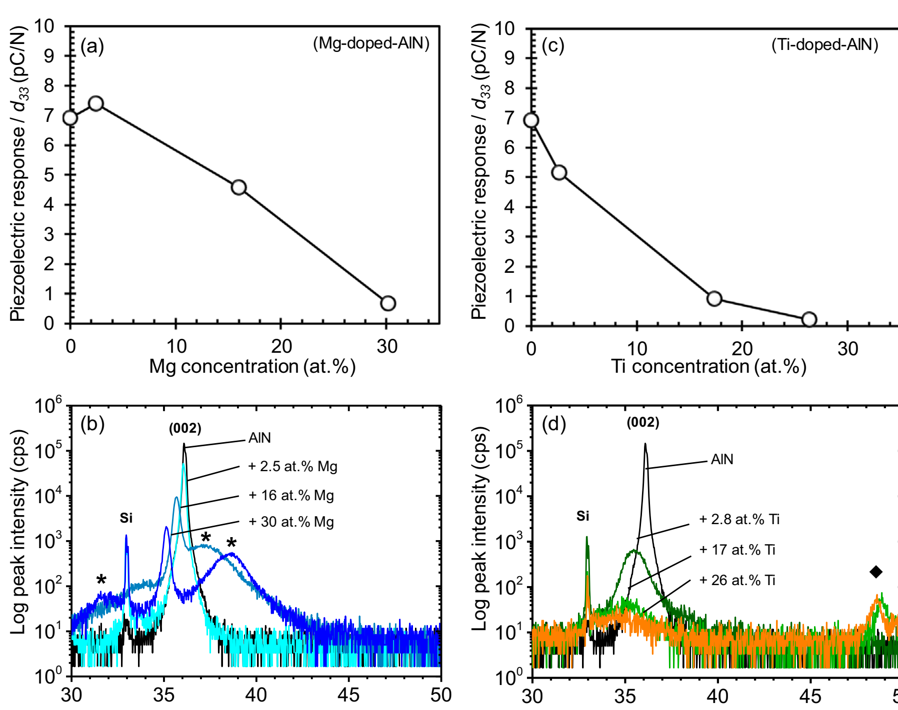

Fig. 1. The effect of Mg concentration on (a) the piezoelectric response (*d33*) and (b) the XRD spectra of Mg-doped-AlN thin films as well as the effect of Ti concentration on (c) the piezoelectric response (*d33*) and (d) the XRD spectra of Ti-doped-AlN thin films. (Fig. 1(a) and (b) is modified from [11] with permission, Copyright Elsevier 2018).