First-Principles Study of Piezoelectric Properties and Bonding Analysis in (Mg, X, Al)N Solid Solutions (X = Nb, Ti, Zr, Hf)

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ABSTRACT: The enhancement mechanism of piezoelectric properties by codoping Mg + X (X = Nb, Ti, Zr, Hf) into aluminum nitride (AlN) was investigated by first-principles calculations. Theoretically, the piezoelectric constant ($d_{33}$) can be increased when the elastic constant ($C_{33}$) is decreased and the piezoelectric stress constant ($\epsilon_{33}$) is increased. All components of $\epsilon_{33}$, which consists of the clamped $\epsilon_{33}$, the Born effective charge ($Z_{33}$), and the strain sensitivity ($du/de$) of the internal parameter, were improved by the addition of Mg + X into AlN. The decrease in $C_{33}$ and the increase in $du/de$ that were observed in Mg + X-codoped AlN indicate the occurrence of elastic softening which was considered to be influenced by changes in the interatomic bond in the wurtzite structure. The bonding analysis of metal–nitrogen (Me–N) pairs in the Mg + X-codoped AlN system which was carried out by crystal orbital Hamilton populations showed that the covalent bonding (Me–N) was weaker than in pure AlN. Therefore, this weaker covalent bond is considered to be one of the origins of the elastic softening. Similar phenomena were also found for Sc-doped AlN which has higher piezoelectric response than that of pure AlN.

1. INTRODUCTION

Aluminum nitride (AlN), which has a wurtzite structure, exhibits piezoelectricity which enables it to be used in thin film bulk acoustic wave resonators for wireless telecommunication devices.1–3 Improvement in the piezoelectric properties of AlN is highly desired for future evolution of communication systems. So far, the highest piezoelectric response has been reported for Sc-doped AlN solid solutions.4,5 Piezoelectric response largely increases as the amount of Sc increases which made it a promising material to be put into practical use as a frequency filter for the fifth-generation mobile communication systems. However, there is a problem in terms of cost since Sc is a relatively expensive element for industrial manufacturing. Therefore, alternative additional elements have been searched into AlN, for example, resulted in comparable piezoelectric properties for Sc-doped AlN.6,7 The similar structural change has been observed in Ta- or Cr-doped AlN solid solutions where the enhancement of piezoelectric response has been also obtained.7,9 Therefore, it has been pointed out that there is the relationship between the decrease in the $c/a$ and the enhancement of piezoelectric response.

Experiments and theoretical calculations have confirmed that codoping Mg + X (X = Ti, Zr, Hf, Nb) into AlN which resulted in higher $d_{33}$ also exhibited a decrease in the $c/a$ as well as $C_{33}$. However, the detailed mechanism of piezoelectric property enhancement, particularly with regards to $Z_{33}$ and $du/de$, has not been investigated. Furthermore, the elastic softening is also an important factor which is thought to be involved in changing the interatomic bond but has never been discussed in detail for Mg + X-codoped AlN. On the other hand, the crystal orbital Hamilton population (COHP) analysis has been extensively used to evaluate electron sharing in interatomic bonds.21,22 Therefore, COHP analysis is considered to be a suitable method for the AlN-based system which is constructed by covalent bonding. Given the importance of this material, evaluating those factors for the case of Mg + X-codoped AlN is expected to provide a meaningful insight for future materials design.

In the present work, we evaluate the piezoelectric properties of the wurtzite structure in Mg + X-codoped AlN by first-

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principles calculations and compare them with the case of Sc-doped AlN. In addition, the relationship between elastic softening and interatomic bonds with the corresponding piezoelectric response was investigated by COHP analysis.

2. RESULTS AND DISCUSSION

2.1. Piezoelectric Properties. The calculated and experimental results of lattice parameters are listed in Table 1. Figure 1 shows the supercell of Mg + X-codoped AlN (X = Nb, Ti, Zr, Hf) in these calculations. The orange, green, blue, and gray spheres indicate Mg, X, Al, and N, respectively. In the case of Sc-doped AlN, Mg and X sites were replaced by Sc.

The reported piezoelectric constants are measured with different concentrations in Mg + X-codoped AlN, ranging from a concentration as low as 5 mol % to as high as 20%. Some of this requires a large sized supercell. Because calculating a large supercell will raise the computational cost, we decided to fix the concentration at 12.5 mol %. The maximum difference between the concentration of dopants used in the calculation and that observed in the experiments is 8%. The calculated $d_{33}$ is in good agreement with the experimental results.

Figure 3 shows the piezoelectric stress constant ($\epsilon_{33}$) and elastic constant ($C_{33}$) as red and blue bars, respectively. In this work, the calculated piezoelectric stress constant $\epsilon_{33}$ of wurtzite AlN is 1.46 (C/m²). This value is relatively close with that reported by Dreyer et al. (1.57). In addition, our calculated $\epsilon_{33}$ and $C_{33}$ of wurtzite AlN are relatively consistent with the reported values where $\epsilon_{33}$ and $C_{33}$ have been calculated as 1.29–1.80 (C/m²) and 354–387 (GPa). It is confirmed that addition of either Sc or Mg + X into AlN results in lower $\epsilon_{33}$ compared with pure AlN. On the other hand, $\epsilon_{33}$ is increased by the addition of either Sc or Mg + X. Therefore, the origin of improvement in the piezoelectric properties of Mg + X-codoped AlN is understood to be similar to that in the case of Sc-doped AlN, which is the decrease of $C_{33}$ and the increase of $\epsilon_{33}$.

The piezoelectric stress constant $\epsilon_{33}$ of the wurtzite structure is described as

$$\epsilon_{33} = \epsilon_{33}^{\text{clamped}} + \epsilon_{33}^{\text{non-clamped}}$$

where $\epsilon_{33}^{\text{clamped}}$ indicates the electronic response to strain and is evaluated by fixing the internal atomic coordinates at their equilibrium positions. $\epsilon_{33}^{\text{non-clamped}}$ changes in the internal coordinates, where $e$ is the (positive) electron charge, $a$ is the equilibrium lattice constant, $Z_{33}$ is the Born effective charge in units of $e$, and $\epsilon$ is the macroscopic applied strain. The internal parameter $u$ is the ratio between the lattice constant $c$ and the metal—nitrogen distance along the $c$-axis in the wurtzite structure. The calculated results of these terms are shown in Figure 4a–d. Figure 4e depicts the wurtzite structure with the internal parameter $u$.

It is revealed that the $\epsilon_{33}^{\text{clamped}}$ of Mg + X-codoped AlN is higher than that of AlN which leads to greater $\epsilon_{33}$. However, Sc-doped AlN does not have the same behavior since the value

![Figure 1. Crystal structure of Mg + X (X = Nb, Ti, Zr, Hf)-codoped AlN.](image1)

![Figure 2. Calculated and experimental piezoelectric constants $d_{33}$ of several AlN-based compounds. The green and orange bars indicate the calculated and experimental results, respectively.](image2)

![Figure 3. The calculated piezoelectric stress constants ($\epsilon_{33}$) and elastic constants ($C_{33}$) of several AlN-based compounds are shown in red and blue bars, respectively.](image3)
of $\varepsilon^\text{clamped}_{33}$ is lower than that of AlN. Under nonclamped conditions, $Z_{33}$ and $d\varepsilon/d\varepsilon$ values of Sc-doped AlN and Mg + X-doped AlN were larger than that of pure AlN. The increase in $d\varepsilon/d\varepsilon$ is particularly large (>10%), which may greatly enhance $\varepsilon^\text{non-clamped}_{33}$. It is considered that such behaviors were influenced by the elastic softening metal–N bond since $d\varepsilon/d\varepsilon$ indicates the change in the metal–N bond length on stress loading along the c-axis direction. Therefore, elastic softening is an important factor for the improvement of $d_{33}$ not only in Sc-doped AlN but also in Mg + X-codoped AlN.

### 2.2. Bonding Analysis

Although AlN is known to be a covalent compound, the change in the bonding characteristic due to the substitution of Al with other elements is predicted to affect the elastic softening of the wurtzite structure. Therefore, the nature of covalent bonding in metal–N pairs is further studied by COHP analysis.

![Figure 4](image1.png)

Figure 4. Several components of $\varepsilon_{33}$, (a) the clamped $\varepsilon_{33}$, (b) the nonclamped $\varepsilon_{33}$, (c) the 33 components of the Born effective charge $Z_{33}$, and (d) the strain sensitivity of the internal parameter $d\varepsilon/d\varepsilon$ for several AlN-based compounds. (e) Wurtzite structure with the internal parameter $u$ which indicates the ratio between the lattice constant $c$ and the metal–nitrogen distance along the c-axis.

![Figure 5](image2.png)

Figure 5. COHP curves of various metal–N pairs in the (a) Al$_{16}$N$_{16}$ (b) Sc$_2$Al$_{14}$N$_{16}$ (c) MgNbAl$_{14}$N$_{16}$ (d) MgTiAl$_{14}$N$_{16}$ (e) MgZrAl$_{14}$N$_{16}$ (f) MgHfAl$_{14}$N$_{16}$ system. The Fermi energy ($E_F$) is indicated by vertical dashed lines.

![Figure 5a-f](image3.png)

Figure 5a–f show the calculated results of COHP for each metal and nitrogen in AlN, Sc-doped AlN and Mg + X-codoped AlN. In these figures, the horizontal axis is energy based on the Fermi energy $E_F$ and the vertical axis is COHP. For COHP, the negative region represents the bonding orbits and the positive region indicates the contribution from the antibonding orbits. Regarding Al–N and Mg–N pairs from Figure 5a–f, bonding orbitals are observed to be filled below $E_F$. The metal–N bond strength is evaluated by the integrated COHP (ICOHP) and those values are listed in Table 2. A lower the ICOHP value corresponds with the stronger covalent bond. The similar ICOHP values of Al–N in AlN, Sc-doped AlN and Mg + X-codoped AlN suggest similar bond strength of Al–N in all the calculated compound systems. However, ICOHP values of Mg–N were found to be higher than Al–N in Mg + X-codoped AlN which indicate that the bond strength of Mg–N is weaker than that of Al–N. This may be due to the
The piezoelectric properties of Mg + X-codoped AlN (X = Nb, Ti, Zr, Hf) were evaluated by first-principles calculations. The piezoelectric constant ($d_{ij}$) increases due to the decrease of the elastic constant $C_{ij}$ and the increase of the piezoelectric stress constant $e_{ij}$. All components of $e_{ij}$ which are the clamped $e_{ij}$, the Born effective charge $Z_{ij}$, and the strain sensitivity $du/dE$ of the internal parameter, were improved by substituting Al with Mg + X. The decrease in $C_{ij}$ and the improvement in $du/dE$ indicate an occurrence of elastic softening in Mg + X-codoped AlN. A weaker covalent bonding between Mg–N and X–N was found by COHP analyses and it is considered to take an important role in promoting the elastic softening for Mg + X-codoped AlN. Moreover, the origin of decrease in the $c/a$ ratio regarding Sc-doped AlN and Mg + X-codoped AlN is thought to be because of the weaker covalent bonding.

### 4. COMPUTATIONAL DETAILS

The structure models of AlN solid solution were constructed by the special quasirandom structures method which is performed by the alloy theoretic automated toolkit based on Monte Carlo simulated annealing method. The size of the supercell was $2 \times 2 \times 2$ (32 atoms) of the wurtzite structure, in which Mg and X (X = Ti, Zr, Hf, Nb) substitute for Al sites. Figure 1 shows the supercell of Mg + X-codoped AlN in the present work. The orange, green, blue, and gray spheres indicate Mg, X, Al, and N, respectively. In the case of Sc-doped AlN, Mg and X sites were replaced by Sc. The chemical composition of the supercell was fixed as MgXAl$_{14}$N$_{16}$ and Sc$_4$Al$_{14}$N$_{16}$ since the enhanced piezoelectric response was confirmed to be found around this composition.

The lattice relaxation was performed with the Vienna Ab initio Simulation Package code (VASP) which is based on density functional theory. The exchange and correlation functions were given by the generalized gradient approximation, as proposed by Perdew et al. We employed Blochl’s projector-augmented wave method as implemented by Kresse and Joubert. The Monkhorst–Pack method is used to set the k-point mesh. The structure optimizations were performed with a $5 \times 5 \times 3$ mesh for k-point sampling with a cutoff energy of 500 eV. The elastic coefficient and piezoelectric stress tensors were evaluated from phonon and dielectric response calculations performed from finite differences and density functional perturbation theory, respectively. The convergence criterion for the electric self-consistency loop was $10^{-6}$ eV in all calculations. Chemical bonding analyses were performed by the COHP method which is implemented in the LOBSTER code.

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