<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Acoustic properties of co-doped AlN thin films at low temperatures studied by picosecond ultrasonics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Nagakubo, Akira; Arita, Mari; Yokoyama, Tsuyoshi et al.</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Japanese Journal of Applied Physics. 2015, 54(7), p. 07HD01-1-07HD01-4</td>
</tr>
<tr>
<td><strong>Version Type</strong></td>
<td>AM</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="https://hdl.handle.net/11094/84531">https://hdl.handle.net/11094/84531</a></td>
</tr>
<tr>
<td><strong>rights</strong></td>
<td>© 2015 The Japan Society of Applied Physics.</td>
</tr>
<tr>
<td><strong>Note</strong></td>
<td></td>
</tr>
</tbody>
</table>

_Osaka University Knowledge Archive : OUKA_

https://ir.library.osaka-u.ac.jp/

Osaka University
Acoustic properties of co-doped AlN thin films at low temperatures studied by picosecond ultras��

Akira Nagakubo, Mari Arita, Tsuyoshi Yokoyama, Satoru Matsuda, Masanori Ueda, Hirotsugu Ogi, and Masahiko Hiroa

1. Introduction

Aluminum nitride (AlN) is an important piezoelectric material and used for film-bulk acoustic resonators (FBARs) in various wireless devices. Although AlN operates at high temperatures, its low piezoelectricity has been desired to be improved. Other group III nitrides and many transition-metal nitrides have been studied for alternative materials because of their outstanding physical properties. Takeuchi, for example, found that there is a metastable wurtzite structure in ScN and suggested the possibility of fabrication of wurtzite Sc-doped AlN using a first-principle calculation. Akiyama et al. succeeded in synthesizing wurtzite Sc$_{0.5}$Al$_{1-x}$N with $x < 0.5$ and found that their piezoelectric constants $d_{33}$ were larger than that of AlN at least by a factor 5. The piezoelectricity enhancement was also confirmed by a first-principle calculation, and the increment of electromechanical coupling constant for ScAlN was also confirmed in an FBAR. However, Sc is an expensive element, and it is not suitable for the mass production. Other doping elements have been, therefore, investigated; Yokoyama et al. proposed (Mg$_{0.5}$Zr$_{0.5}$)$_2$Al$_{1-x}$N and (Mg$_{0.5}$Hf$_{0.5}$)$_2$Al$_{1-x}$N and indicated the enhancement in $d_{33}$ by a factor approximately 3 at $x = 0.13$. However, their important acoustic properties such as sound velocities, elastic constants, and their temperature coefficients remain unclear.

In this study, we measure the longitudinal-wave velocity along $c$-axis ($v_c$) of (Mg$_{0.5}$Zr$_{0.5}$)$_2$Al$_{1-x}$N and (Mg$_{0.5}$Hf$_{0.5}$)$_2$Al$_{1-x}$N thin films between 190 and 300 K and their temperature coefficients using picosecond ultrasound spectroscopy. The sound velocity governs resonant frequencies of FBARs, and the temperature coefficient of velocity (TCV) determines the temperature stability of the resonant frequency. Especially, the out-of-plane elastic constant ($C_{33}$) is the most important parameter in FBARs because it determines the through-thickness resonant frequencies. However, accurate measurement of $C_{33}$ for a thin film is never straightforward; thin films exhibit different mechanical properties from corresponding bulk specimens. Therefore, it is important to measure $C_{33}$ and TCV directly for a deposited thin film, and picosecond ultrasound spectroscopy can measure the out-of-plane sound velocity within 0.5% accuracy where the film thickness is three times larger than the wavelength. Using this method, we have revealed the elastic properties of oxides films and unusual elasticity of nm-order metallic thin films. In this study, we observe Brillouin oscillation and pulse echo signals within thin films for the same specimens. At room temperature, we determine sound velocity from Brillouin-oscillation method within 0.26% standard deviation (SD) using measured refractive index by ellipsometry. Measured $C_{33}$ of pure AlN-thin film agrees with the reported bulk value. $C_{33}$ and $Q$ values decrease significantly by doping Mg, Zr, and Hf elements. Determined TCV of pure AlN thin film from Brillouin-oscillation and pulse-echo methods agree with each other.

2. Experimental

We developed the optics for the picosecond ultrasound spectroscopy measurements at cryogenic temperature. We used a Ti/sapphire femtosecond pulse laser whose wavelength, repetition rate, and band width are 800 nm, 80 MHz, and 7.0 nm, respectively. Using a half-wavelength plate and a polarization beam splitter, we divided the source light pulse into pump and probe light pulses, which excite and detect an ultrasonic wave. We controlled the delay line of the pump light pulse using two corner reflectors and a stage controller, and modulate the pump light pulses as 100 kHz to improve signal-to-noise ratio using a lock-in amplifier. The wavelength $\lambda$ of the probe light is converted into 400 nm by a second harmonic generator, making it possible to distinguish the pump and probe lights by a dichroic mirror. The pump and probe lights are normally incident to the specimen surface through an objective lens (x20) and the glass window of a cryostat head.

The pump light pulse excites an ultrasharp strain pulse, which propagates in the thickness direction and diffracts the time-delayed probe light pulse backward, leading to interference between the reflected probe light at the surface and the diffracted probe light. The reflec-

*E-mail address: ogi@me.es.osaka-u.ac.jp
Results and Discussion

We prepared a pure AlN thin film, two 
\((\text{Mg}_{0.5}\text{Zr}_{0.5})_{x}\text{Al}_{1-x}\text{N}\) thin films \((x = 0.070 \text{ and } 0.126)\), and three 
\((\text{Mg}_{0.5}\text{Hf}_{0.5})_{x}\text{Al}_{1-x}\text{N}\) thin films \((x = 0.058, 0.088, \text{ and } 0.112)\) on Si (100) substrates using radio frequency reactive sputtering method. Their film thicknesses are about 1 \(\mu\)m. Details of the specimens are shown in Table I. We additionally deposited 10-nm Al thin films on the surface as ultrasonic transducers, which convert the pump light pulse into the acoustic pulse.

3. Results and Discussion

We show a typical observed signal for the pure AlN thin-film specimen in Fig. 1 (a), where the thermal-decay background was subtracted by a polynomial function to extract thermal decay. To determined sound velocity from pulse-echo signals, we used four echoes and calculate the slope as shown in (c).

3. Results and Discussion

We prepared a pure AlN thin film, two 
\((\text{Mg}_{0.5}\text{Zr}_{0.5})_{x}\text{Al}_{1-x}\text{N}\) thin films \((x = 0.070 \text{ and } 0.126)\), and three 
\((\text{Mg}_{0.5}\text{Hf}_{0.5})_{x}\text{Al}_{1-x}\text{N}\) thin films \((x = 0.058, 0.088, \text{ and } 0.112)\) on Si (100) substrates using radio frequency reactive sputtering method. Their film thicknesses are about 1 \(\mu\)m. Details of the specimens are shown in Table I. We additionally deposited 10-nm Al thin films on the surface as ultrasonic transducers, which convert the pump light pulse into the acoustic pulse.

Fig. 1. (a) Observed reflectivity change for the pure AlN specimen and (b) extracted pulse echo using equation (2). We used a polynomial function to extract thermal decay. To determined sound velocity from pulse-echo signals, we used four echoes and calculate the slope as shown in (c).

The initial small-amplitude and low-attenuation oscillation is the Brillouin oscillation from the AlN thin film. The subsequent high-frequency, larger-amplitude, and higher-attenuation oscillation is that of Si substrate, resulting from higher refractive index, larger piezo-optic constant, and higher extinction coefficient of Si, respectively. We also succeeded in observing the ultrasonic pulse-echo signals around 240 and 470 ps within the thin film, but they are small and buried in the Brillouin oscillations. Therefore, we convert the raw data \(S(t)\) into \(S'(t)\) through the following equation:

\[
S'(t) = \frac{1}{4} S(t + \frac{\tau}{2}) + \frac{1}{2} S(t) + \frac{1}{4} S(t - \frac{\tau}{2}) \quad (2)
\]

where \(\tau\) is the period of a Brillouin oscillation. Using this conversion, we can remove the oscillation component with period \(\tau\). To remove both Brillouin oscillations from the thin film and Si, we applied equation (2) twice for \(\tau_{\text{AIN}}\) and \(\tau_{\text{Si}}\), and obtained the Brillouin-oscillation-free signals as shown in Fig. 1 (b). This signal processing makes the pulse-echo signals clearly visible not only at the surface but also at the film-substrate interface.

We applied this procedures to all specimens as shown in Fig. 2. Except the pure AlN specimen, the second-surface-echo amplitudes were small despite the same film thickness, insisting that attenuation increases by addition of the substitution elements. We can also confirm this attenuation increment from the Brillouin oscillation from the thin films; its amplitude in pure AlN film appears to be undamped. On the other hand, Brillouin-oscillation amplitude of \((\text{Mg}_{0.5}\text{Zr}_{0.5})_{0.126}\text{Al}_{0.874}\text{N}\) film clearly attenuates in 100 ps. Since absorption of probe light in thin films can be neglected for 400-nm wavelength light,\(^{25,26}\) attenuation of the Brillouin oscillation is caused by ultrasound attenuation. The \(Q\) value of FBARs is also very important especially for a higher-frequency range and we found that it decreases by doping elements; addition of Mg and Zr more markedly deteriorates the \(Q\) value. We obtained attenuation coefficient of 109 GHz longitudinal wave in \((\text{Mg}_{0.5}\text{Zr}_{0.5})_{0.126}\text{Al}_{0.874}\text{N}\)
to be 33 ± 15 ns⁻¹, yielding 2.9 ± 1.3 × 10⁵ dB/cm.

Next, we measured \( v_c \) and \( C_{33} \) of all films from their Brillouin oscillations at room temperature. We measured more than 3 different points on each specimen and determined Brillouin-oscillation frequencies using fast Fourier transformation; their SDs were less than 0.26%. Measured \( C_{33} \) and \( v_c \) are shown in Table I and Fig. 3. Reported \( C_{33} \) of pure AlN measured by a Brillouin-scattering method is 402 GPa,²⁷ showing good agreement with our measurement value of 398.2 ± 0.7 GPa. We observed that \( C_{33} \) of the co-doped AlN thin films largely decrease (down to 80%) and this trend is more remarkable in the (Mg₀.₅Zr₀.₅)ₓAl₁₋ₓN films than the (Mg₀.₅Hf₀.₅)ₓAl₁₋ₓN films. On the other hand, the sound velocity of (Mg₀.₅Hf₀.₅)ₓAl₁₋ₓN is smaller than (Mg₀.₅Zr₀.₅)ₓAl₁₋ₓN films, reflecting larger atomic mass of Hf.

Then, we measure TCVs of the films. Brillouin-oscillation method is a promising method to measure the longitudinal sound velocity since it does not depend on specimen shape or dimensions. Furthermore, it shows a higher signal-to-noise ratio comparing to Brillouin scattering method due to the excited coherent strain pulse by the pump light pulse.²⁸ However, this method requires the refractive index in an analogous way with the Brillouin-scattering method; Watanabe et al. measured refractive index of 9.23-μm-thick AlN between 300 and 800 K and found that refractive index of AlN linearly increases with temperature in 38 ppm/K for 400-nm wavelength light,²⁹ and we assumed that \( dn/dT \) of all specimens are constant to be 38 ppm/K between 190 and 300 K. We show the measured temperature dependence of \( v_c \) of pure AlN thin film in Fig. 4 and obtained TCV of all thin films in Fig. 5. Absolute value of TCV slightly increases by doping Mg, Zr, and Hf. Measured \( v_c \) of (Mg₀.₅Zr₀.₅)ₓAl₁₋ₓN thin film shows wider distribution (0.38% at most), yielding larger error bars of TCV. TCV of (Mg₀.₅Zr₀.₅)ₓAl₁₋ₓN and (Mg₀.₅Hf₀.₅)ₓAl₁₋ₓN determined by Brillouin-oscillation method should be considered substitution-elements dependence of \( dn/dT \).³⁰
ever, we would obtain same value within our measurements error whether we consider it or not.

We also measured temperature dependence of sound velocity of pure AlN thin film using the pulse-echo method as shown in Fig. 4. Other films prevented us from determining the velocity accurately because of larger attenuation. Thermal expansion coefficients of AlN around room temperature are about 3 ~ 5 ppm/K. We also estimated Poisson’s effect; since AlN thin film and Si substrate have different thermal expansion coefficient, the film thickness changes due to not only thermal expansion of itself but also that of substrate. We assumed that the film is thin enough comparing to the substrate and its in-plane displacements are restricted by the substrate, inducing a thermal strain \( \varepsilon_{11} = (\alpha_0 - \alpha_{AlN}) \Delta T \), where \( \Delta T \) is temperature change from room temperature, and \( \alpha_0 \) and \( \alpha_{AlN} \) are thermal expansion coefficients of Si and AlN along \( \alpha \)-axis, respectively. Then, the total film-thickness change is

\[
\left( \alpha_{AlN} - \frac{2C_{13}}{C_{33}} (\alpha_0 - \alpha_{AlN}) \right) d_0 \Delta T
\]

\( (3) \)

where \( \alpha_{AlN} \) is linear thermal-expansion coefficient of AlN along \( \alpha \) axis, \( C_{13} \) and \( C_{33} \) are the elastic constants of AlN, and \( d_0 \) is the film thickness at room temperature, respectively. Equation (3) yields 2.8 ppm/K at room temperature.

\( 0 \)