<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Zero temperature coefficient of sound velocity in vitreous silicon oxynitride thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Citation</strong></td>
<td>Applied Physics Letters. 114(25) P.251905-1-P.251905-5</td>
</tr>
<tr>
<td><strong>Issue Date</strong></td>
<td>2019-06-25</td>
</tr>
<tr>
<td><strong>Text Version</strong></td>
<td>publisher</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/11094/83932">http://hdl.handle.net/11094/83932</a></td>
</tr>
<tr>
<td><strong>DOI</strong></td>
<td>10.1063/1.5098354</td>
</tr>
<tr>
<td><strong>rights</strong></td>
<td>Copyright 2019 Author(s). This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. This article appeared in Applied Physics Letters, 114(25), 251905, 2019 and may be found at <a href="https://doi.org/10.1063/1.5098354">https://doi.org/10.1063/1.5098354</a>.</td>
</tr>
<tr>
<td><strong>Note</strong></td>
<td>Osaka University Knowledge Archive : OUKA</td>
</tr>
</tbody>
</table>
Zero temperature coefficient of sound velocity in vitreous silicon oxynitride thin films

Cite as: Appl. Phys. Lett. 114, 251905 (2019); https://doi.org/10.1063/1.5098354
Submitted: 02 April 2019 . Accepted: 05 June 2019 . Published Online: 25 June 2019

Zero temperature coefficient of sound velocity in vitreous silicon oxynitride thin films


ABSTRACT

Vitreous silicon oxide (v-SiO$_2$) shows anomalous phonon properties such as the positive temperature coefficient of velocity (TCV). Variation of the Si–O–Si bond angle between SiO$_4$ tetrahedrons has been recognized to be the key, but the origin of TCV still remains unclear. In this study, we controlled the bond angle by doping nitrogen and measured TCV of vitreous silicon oxynitride thin films with various nitrogen concentrations using picosecond ultrasonics. TCV significantly decreases by adding a small amount of nitrogen, and it shows positive to negative values as the nitrogen concentration increases. We evaluated the bond-angle change by Fourier-transform infrared spectroscopy, which decreases with the increase in the nitrogen content. We also find that the temperature rise in nondoped v-SiO$_2$ decreases the bond angle, leading to an increase in the sound velocity. We then reveal theoretically that the bond-angle change dominates the origin of the positive TCV. This study indicates the existence of a zero-TCV single material, and we discover that the specific content of v-SiO$_{1.71}$N$_{0.19}$ achieves this.
Si–O–Si angle $\theta$ would not be the direct reason for the positive TCV, although their calculation predicted a decrease in the bond angle with the temperature increase.

It is therefore unambiguously important that the bond angle between the tetrahedron units will dominate the unusual properties of v-SiO$_2$. However, there is no systematic study on the correlation between TCV and the bond angle. In this study, to reveal the origin of the positive TCV, we measure sound velocity of vitreous silicon oxynitride (v-SiO$_x$N$_y$) films between 10 and 300 K by picosecond ultrasonics and evaluate the bond-angle change by Raman spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy. Since nitrogen atoms can have three bonds to Si atoms, while oxygen atoms have two bonds, the Si–N–Si bond angle becomes smaller than the Si–O–Si angle $\theta$, so that we can control $\theta$ by doping N into v-SiO$_2$. Because vitreous silicon nitride, v-Si$_3$N$_4$, exhibits negative (usual) TCV, by increasing the N atoms, we will observe a positive-to-negative change of TCV, which provides us with important information on the positive TCV mechanism. Furthermore, this approach will reveal a zero-TCV single material. (Note that achieving the zero-TCV required a composite consisting of a positive TCV material such as v-SiO$_2$ and negative TCV materials.)

We synthesized v-SiO$_x$N$_y$ films on (100) Si substrates by a reactive sputtering method with a Si target under an Ar/N$_2$/O$_2$ atmosphere. We controlled the composition by changing the flow rates of Ar, N$_2$, and O$_2$ gases; it was determined by the X-ray photoelectron spectroscopy (XPS) method as follows: The binding energy of the N$s$ and O$s$ signals was compared with the values of N$_2$ and O$_2$ as standards. Here, we define $N_x$, as the nitrogen ratio $N_x = N/(O + N)$. We measured the mass density $\rho$, the longitudinal elastic constant $C_L$, TCV, and $\omega_4$ of each film with reference values. $N_x$ denotes the nitrogen ratio $N_x = N/(O + N)$.

**TABLE I.** Determined mass density $\rho$, sound velocity $v$, longitudinal elastic constant $C_L$, TCV, and $\omega_4$ of each film with reference values. $N_x$ denotes the nitrogen ratio $N_x = N/(O + N)$.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$N_x$</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$v$ (km/s)</th>
<th>$C_L$ (GPa)</th>
<th>TCV (ppm/K)</th>
<th>$\omega_4$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiN$_4$/3</td>
<td>1</td>
<td>3020$^a$</td>
<td>10.206$^b$</td>
<td>314.5$^{+45}_{-45}$</td>
<td>$-21.0^{+45}_{-45}$</td>
<td></td>
</tr>
<tr>
<td>SiO$<em>{1.13}$N$</em>{0.89}$</td>
<td>0.891</td>
<td>2940</td>
<td>10.083</td>
<td>298.3</td>
<td>$-15.3$</td>
<td>886.1</td>
</tr>
<tr>
<td>SiO$<em>{0.36}$N$</em>{0.96}$</td>
<td>0.726</td>
<td>2910</td>
<td>9.877</td>
<td>282.6</td>
<td>$-14.4$</td>
<td>898.2</td>
</tr>
<tr>
<td>SiO$<em>{1.67}$N$</em>{0.33}$</td>
<td>0.552</td>
<td>2810</td>
<td>9.401</td>
<td>248.3</td>
<td>$-24.1$</td>
<td>960.5</td>
</tr>
<tr>
<td>SiO$<em>{0.94}$N$</em>{0.63}$</td>
<td>0.402</td>
<td>2680</td>
<td>8.823</td>
<td>208.6</td>
<td>$-14.2$</td>
<td>974.4</td>
</tr>
<tr>
<td>SiO$<em>{1.24}$N$</em>{0.44}$</td>
<td>0.260</td>
<td>2690</td>
<td>8.342</td>
<td>187.2</td>
<td>$-8.14$</td>
<td>996.7</td>
</tr>
<tr>
<td>SiO$<em>{0.71}$N$</em>{0.19}$</td>
<td>0.101</td>
<td>2510</td>
<td>7.496</td>
<td>140.1</td>
<td>$-0.64$</td>
<td>1030.9</td>
</tr>
<tr>
<td>SiO$<em>{0.77}$N$</em>{0.11}$</td>
<td>0.059</td>
<td>2390</td>
<td>7.124</td>
<td>121.3</td>
<td>11.8</td>
<td>1041.4</td>
</tr>
<tr>
<td>SiO$<em>{0.93}$N$</em>{0.07}$</td>
<td>0.035</td>
<td>2370</td>
<td>6.837</td>
<td>110.8</td>
<td>56.5</td>
<td>1048.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0</td>
<td>2220$^c$</td>
<td>5.967$^d$</td>
<td>79.0$^{+45}_{-45}$</td>
<td>69.9$^{+45}_{-45}$</td>
<td>1064.5$^d$</td>
</tr>
</tbody>
</table>

$^a$Reference 17.
$^b$Reference 27.
$^c$Reference 25.
$^d$Reference 26.

Increases, indicating that the averaged bond angle becomes smaller. We confirmed that these films do not show any crystalline phases with X-ray diffraction (XRD) spectra as shown in the supplementary material (Fig. S3), where only the Si (100) peaks for Co-K$\alpha$ and Co-K$\beta$ X-ray appear except for noise signals.

We measured the longitudinal-wave sound velocity $v$ by picosecond ultrasonics, which is the pump-probe laser ultrasonics with a femtosecond pulse laser. We used a titanium/sapphire pulse laser whose wavelength and repetition rate were about 800 nm and 80 MHz, respectively. The light pulse was divided into pump and probe light pulses by a polarization beam splitter. The pump light path was controlled by corner reflectors and a stage controller, and we modulated the pump light at 100 kHz for the lock-in-amplifier detection. The wavelength of the probe light was converted into 400 nm by a second harmonic generator. Both light normally entered a specimen in a cryostat through an objective lens and a glass window.

We deposited Al thin films on the specimens as the transducer, which absorbed pump light pulses and excited strain pulses. The strain pulse diffracts the probe light backward, whose wave vector satisfies Bragg’s condition. The diffracted light interferes with reflected light from the surface, and therefore, total intensity is modulated with strain-pulse propagation as the frequency of $f = 2n\lambda$, where $\lambda$ is the wavelength of the probe light and $n$ is the refractive index of the specimen. This oscillation is called Brillouin oscillation. We measured $n$ of the v-SiO$_x$N$_4$ films and $\lambda$ by ellipsometry and a spectrometer, respectively.

We show waveforms observed at room temperature in Fig. 2(a). The strain pulse generated at the surface propagates in a v-SiO$_x$N$_y$ film, causing the Brillouin oscillation, and reaches the Si substrate around 100–180 ps. The transmitted strain pulse causes the Brillouin oscillation in Si. The reflected strain pulse propagates in the v-SiO$_x$N$_y$ film backward, reflects at the surface, and reaches the Si substrate again as shown in Figs. 2(b)–2(d). At room temperature, we determined the sound velocity from the Brillouin-oscillation frequency by applying...
fast Fourier transform and obtained the longitudinal-wave elastic constant $C_L = \rho v^2$, which is shown in Table I. The sound velocity is depicted in Fig. 1(a), together with reference values. As the nitrogen ratio increases, the mass density increases because of reduction of the bond angles between polyhedrons (angles of O-Si-O, O-Si-N, and N-Si-N), leading to the decrease in the averaged atomic distance. This causes the significant increase in the elastic modulus. We here focus on the O–Si–O bond angle, because it is a representative characteristic related to changes in those bond angles, and it is accurately obtainable by the FT-IR and Raman spectroscopy.

In measuring TCV, we determined the sound velocity change $\Delta v$ by the pulse-echo method not by the Brillouin oscillation, because the velocity measurement is negligible; the thermal expansion coefficient of the substrate. This evaluation, for example, estimates the film-thickness change of 0.03% or less for a v-SiO$_2$ film-thickness change of 0.03% or less for a v-SiO$_2$ film deposited on a substrate is modified as $t_{\text{Sub}} = COt_{\text{film}}$, where $t_{\text{Sub}}$ is the thermal expansion coefficient of the substrate.

The arrow in Figs. 2(b)–2(d) indicates the second arrival time to the Si substrate. (We chose a clearly visible peak of the signal to determine the arrival time. A small difference in the sampling point has a negligible influence in determining TCV because it is derived from the relative velocity change.) We then measured the one-and-half round trip time and determined $\Delta t$ from room temperature as shown in Fig. 3. A pure v-SiO$_2$ film shows positive TCV, but TCV of the v-SiO$_2$N$_x$ film decreases as the nitrogen ratio $N_x$ increases. We determined TCV using data between 200 and 300 K, which are shown in Table I and Fig. 1(b). As the nitrogen content increases, the TCV value changes from positive to negative as expected. However, the zero-TCV film is achieved at a very low $N_x$ value ($N_x \approx 0.1$), which is unexpected behavior because the absolute value of TCV of v-SiO$_2$ is three-times higher than that of v-SiN (Fig. 1(b)), and a large amount of nitrogen was expected to achieve the zero TCV. TCV is, thus, highly affected by the addition of nitrogen atoms near $N_x = 0$, and we attribute this unusual TCV behavior to the bond-angle temperature coefficient as shown below.

To reveal the origin of the positive TCV of v-SiO$_2$, we measured the Raman spectrum of a bulk v-SiO$_2$ between 77 and 373 K (Fig. S4). Tetrahedral glasses have four representative phonon modes ($\omega_1$, $\omega_2$, $\omega_3$, and $\omega_4$), which significantly depend on the bond angle $\theta$. Among them, we used the $\omega_3$ and $\omega_4$ modes to evaluate the bond-angle change: the $\omega_1$ mode is close to a defect line $D_1$ which arises from the symmetric stretch and irregular planar glass network, and the $\omega_2$ peak overlaps on the broad $\omega_1$ peak (Fig. S4). The frequencies of $\omega_3$ and $\omega_4$ modes are given by

$$\omega_3 = \sqrt{\frac{C(1 + \cos \theta)}{m_O} + \frac{4C}{3m_Si}}$$

$$\omega_4 = \sqrt{\frac{C(1 - \cos \theta)}{m_O} + \frac{4C}{3m_Si}}$$

where $m_O$ and $m_Si$ are the mass of O and Si atoms, respectively, and $C$ is the spring constant for the Si–O bond stretching. Both $\omega_3$ and $\omega_4$ peaks exhibit transverse-optical (TO) and longitudinal-optical (LO) modes. We determined their phonon frequencies for the $\omega_3$ mode using the double-peak function-fitting method. On the other hand, the TO and LO modes of the $\omega_4$ peak are clearly separated, and we
measured the phonon frequency of the TO-$\omega_3$ mode. With the temperature increase, phonon frequencies of the $\omega_3$ and $\omega_4$ modes increase and decrease, respectively, as shown in Fig. 4(a). We inversely calculated the bond angle $\theta$ and the spring constant $C$ from the measured phonon frequencies of the TO-$\omega_3$ mode (lower $\omega_3$ mode) and TO-$\omega_4$ mode as shown in Fig. 4(b), which agree with those reported with $\sim$5% or less. We find that they decrease as temperature increases. The spring constant, thus, decreases as temperature increases as like usual materials, and, therefore, the decrease in $\theta$ should cause the sound-velocity increase with the temperature increase.

In our previous study, we made several v-SiO$_2$ films with different sputtering powers and found that $v$ increases as $\theta$ decreases. Importantly, the bond-angle change caused by temperature and sputtering power leads to an identical sound-velocity change: In the previous measurement, $dv/d\omega_4$ is estimated to be $-0.29\ m^2/s$. On the other hand, the reported TCV ($dv/dT$) and the temperature dependence of the $\omega_4$ frequency $d\omega_4/dT$ yield the $dv/d\omega_4$ value of $-0.25\ m^2/s$. They well agree with each other, indicating that the sound velocity change is principally governed by the change in the Si–O–Si bond angle.

We consider that this structural change governs TCV of the v-SiO$_2$N$_x$ film. To evaluate the bond-angle change, we measured the FT-IR spectra of the films. We observed superimposed spectra of Si–N and Si–O absorption peaks around 1000 cm$^{-1}$ and determined the peak frequency of the $\omega_4$ mode by the multipeak function-fitting method [Figs. S5(a) and S5(b)]. With an increase in the nitrogen ratio $N_x$, the peak frequency linearly decreases [Fig. S5(c)], which corresponds to a gradual decrease in the bond angle $\theta$. We reveal that the unexpected nitrogen-ratio dependence of TCV is explained by the temperature coefficient of the bond angle $d\theta/dT$: by differentiating $\omega_4^4$ [Eq. (2)] with respect to $T$, $d\theta/dT$ becomes

$$
\frac{d\theta}{dT} = \frac{m_O}{C \sin \theta} \left( 2 \omega_4 \frac{d\omega_4}{dT} - \left( 1 - \frac{m_N}{m_O} \right) \frac{4}{3m_O} \frac{dC}{dT} \right).
$$

and we calculated $d\theta/dT$ values of v-SiO$_2$N$_x$ films using $dC/dT$ and $d\omega_4/dT$ values of pure v-SiO$_2$ in Fig. 4. (These temperature coefficients were determined using experiments between 190 and 340 K.) We show the calculated $d\theta/dT$ values in Fig. 1(b). TCV and $d\theta/dT$ show a similar dependence on the nitrogen ratio $N_x$ and they show a good correlation (inset in Fig. 5).

The bond angle in the v-SiO$_2$N$_x$ film is expected to decrease with the temperature increase as seen in v-SiO$_2$ which contributes to an increase in $v$. However, when the bond angle is already small enough due to the existence of N atoms, the absolute value of its temperature coefficient $|d\theta/dT|$ becomes small, whereas the interatomic bond length becomes larger because of thermal expansion, which contributes to the decrease in $v$. Therefore, the TCV value is determined by the trade-off between the two conflicting mechanisms: the bond-angle change and thermal expansion. The zero-TCV v-SiO$_2$N$_x$ film can then be realized by the exact balance between the two factors. The most important point is that TCV of vitreous SiO$_2$-base materials does not seem to depend on the doped atoms but only on the bond angle temperature coefficient: we show the $\omega_4$-frequency dependence of TCV of v-SiO$_2$N$_x$ and v-SiO$_2$F$_x$ films in Fig. 5. With an increase in the phonon frequency, TCV of the film increases. This behavior can be explained by the temperature coefficient of the bond angle as shown in the inset, where the $d\theta/dT$ value shows a linear correlation with TCV even involving the F-doped films.

To conclude, we synthesized v-SiO$_2$N$_x$ films and measured their sound velocity between 10 and 300 K using time-of-flight measurements using the picosecond ultrasonic technique. Doping N atoms caused an increase in sound velocity and a decrease in TCV. We evaluated the structural change from the TO-$\omega_4$ phonon frequency, which corresponds to the Si–O–Si bond angle. We conclude that the change of the bond angle is the most important parameter for governing TCV of v-SiO$_2$N$_x$ and v-SiO$_2$F$_x$ ($x<0.264$). The temperature increase

![FIG. 4.](image1.png)

![FIG. 5.](image2.png)
leads to a decrease in the bond angle, resulting in positive TCV. However, if it already becomes small enough, it cannot become smaller even with temperature increase, and usual thermal expansion causes a decrease in mass density and sound velocity. Thus, the TCV of $v$-$SiO_N$ decreases in mass density and sound velocity. Thus, the TCV of $v$-$SiO_N$ decreases in mass density and sound velocity. Thus, the TCV of $v$-$SiO_1.71N_0.19$. 

See the supplementary material for XPS, x-ray-reflectivity, XRD, Raman, and FT-IR measurements.

REFERENCES