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Mechanical properties of low- and high-\( k \) dielectric thin films: A surface Brillouin light scattering study

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Surface Brillouin light scattering measurements are used to determine the elastic constants of nanoporous low-\( k \) SiOC:H (165 nm) and high-\( k \) HfO\(_2\) (25 nm) as well as BN:H (100 nm) films grown on Si substrates. In addition, the study investigates the mechanical properties of ultra-thin (25 nm) blanket TiN cap layers often used as hard masks for patterning, and their effects on the underlying low-\( k \) dielectrics that support a high level of interconnected porosity. Depending on the relative material properties of individual component layers, the acoustic modes manifest as confined, propagating, or damped resonances in the light scattering spectra, thereby enabling the mechanical properties of the ultra-thin films to be determined. © 2016 AIP Publishing LLC.

I. INTRODUCTION

Dielectric materials have broad applications ranging from conventional insulators in electrical circuitry to their functionality in active device architectures such as rectifiers, semiconductor transistors, and capacitors. As the microelectronics technology continues to develop, the need for materials with both low- and high-dielectric constants, \( k \), has become more critical. For instance, the continuous decrease in feature sizes and faster speeds in integrated circuits have reached a point where the interconnect signal or resistance-capacitance (RC) delay has become comparable to the transistor gate delay.\(^{1,2}\) Low-\( k \) dielectric materials enable scaling of these devices allowing for the dielectrics to get closer without charge build up and adversely affecting device performance. Similarly, high-\( k \) materials are also playing increasingly important roles. As an example, when the thickness of a component layer scales below 2 nm, the resulting leakage current leads to unwieldy power consumption, and reduced device reliability; high-\( k \) dielectric materials allow for increased gate capacitance without the concomitant leakage effects.\(^{3,4}\)

While these advancements exploit the properties of the dielectric materials to enable integration of different functionalities onto a single platform, there are inherent adverse consequences that often emerge and must be overcome. For example, the integration of low-\( k \) materials in which the traditional silicon dioxide (SiO\(_2\), \( k \approx 3.9 \)) dielectric is replaced by layers with a much lower \( k \) (\(<2.0\)) has been achieved by introducing a methyl group (CH\(_3\)) into the SiO\(_2\) matrix.\(^2\) The ensuing modifications result in a highly porous SiOC:H structure, which in turn adversely affects its mechanical properties.\(^4,13\)

Another important processing step of structures consisting of low-\( k \) materials involves deposition of a thin hard over-layer such as titanium nitride (TiN) to serve as a mask for etching into the porous SiOC:H. While such hard masks are needed to create nano- and microscale patterned structures, their presence, however, could lead to mechanical instabilities or modifications in the underlying low modulus material. Such adverse manifestations have been observed, for example, as undulations and wiggles in the dielectric ridges for trench widths less than 100 nm.\(^{14,15}\)

Materials such as hafnium oxide on the other hand are of interest due to their high dielectric constant (\( k \approx 25 \)) and interface stability with silicon that promotes reduced gate leakage, enhanced breakdown threshold, and increased capacitance density and voltage linearity.\(^{15}\) Similarly, different forms of BN:H have \( k \) values ranging between 4 and 6 (\( >k_{\text{silicon}} \)) and are finding applications as a diffusion barrier or gate dielectric in graphene channel field effect transistor devices due to its higher elastic modulus and wide bandgap.\(^{17,18}\) While the electrical properties of such high-\( k \) materials such as HfO\(_2\) and BN:H have been widely studied, much less is known about their mechanical properties. These properties are important because their elasto-mechanical responses to thermal cycling and the consequences of interfacial and process-driven stresses can affect compatibility of integration, long-term reliability, and device performances. There is thus a growing need to non-destructively determine the structural and mechanical properties of these types of thin, highly functional low- and high-\( k \) material systems.

In this present surface Brillouin scattering (SBS) study, the long wave acoustic phonons and their frequency dispersions are used to non-destructively determine the mechanical properties of individual component dielectric layers. Importantly, SBS results are not skewed by challenges often encountered in more traditional methods at these length scales (\(<200 \text{ nm}\)), where for example, substrate–indenter interactions could be a problem.\(^{19}\) The influence of thin (\(<50 \text{ nm}\)) hard amorphous TiN over-layers deposited over the SiOC:H films (\(<200 \text{ nm}\)) on the individual elastic constants, Poisson’s ratio, and Young’s modulus of TiN/SiOC:H/SiO\(_2\)/Si multilayer structures is investigated by probing the associated phonon modal frequencies and their coupling efficiency to photons. While significant reductions

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(compared to the SiO$_2$ matrix) in the mechanical properties due to increased porosity of the SiOC:H layers are determined, the TiN cap layer (despite its amorphous character and resulting lowered modulus) is also found to affect the elastic properties of the underlying porous dielectric layer.

Two classes of ultra-thin (<100 nm) high-k films—HfO$_2$ and a-BN:H—are also investigated. While low lying Rayleigh and Sezawa modes are clearly evident, in agreement with the simulated phonon density of states and relative mechanical properties of individual layers, it is found that the confined acoustic resonances associated with these layers are, however, damped. For instance, high frequency (>50 GHz) acoustic resonances confined to ultrathin (<100 nm) HfO$_2$ films are strongly damped at room temperature and will thus impact phonon lifetimes and thermal management in the associated nano-electronics. In contrast, although some degree of damping is still observed, the acoustic impedance mismatches lead to less mode damping in lamellar structures of a-BN:H layers on bulk Si.

II. BACKGROUND AND EXPERIMENTAL DETAILS

A. Surface Brillouin scattering

We have employed surface Brillouin scattering (SBS) of light, an experimental technique for measuring the vibrational spectrum of sub-micron supported layers and multilayers (thickness d), and thereby determining their elastic properties.$^{20-22}$ A laser beam of frequency $\omega_0$ and wave number $k_0 = \omega_0/c$ is incident on the highly polished surface of a sample at an angle $\theta$ to the surface normal, and the back-scattered light, shifted in frequency by $\omega$, is collected and analyzed, see Fig. 1. Our measurements were carried out using 200–300 mW of p-polarized 532 nm laser light focused to a spot size of 30 µm on the surface of the sample, with $\theta$ in the angular range ($5^\circ \leq \theta \leq 70^\circ$.$^{23}$ A six-pass tandem Fabry–Perot interferometer was used to disperse the light. For an opaque solid, the scattering is caused by dynamic fluctuations in the surface profile resulting from the thermal equilibrium distribution of bulk and surface phonons having wave vector component $k_{||} = 2k \sin \theta$ at the surface. Through the fluctuation-dissipation theorem, it follows that the scattering cross section is given by$^{20,21}$

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{AT}{\omega} \text{Im} G_{33}(k_{||}, \omega; z = 0),$$

where $A$ is a constant that depends on the scattering geometry and the frequency and polarization of the light, and $G_{33}(k_{||}, \omega)$ is the surface elastodynamic Green’s function for force and displacement in the $3$ direction normal to the surface. Where there is some penetration of the light into the films, a certain amount of elasto-optic scattering takes place, and the other components, $G_{ij}(k_{||}, \omega)$, of the Green’s tensor are brought into play.

The calculation of $G_{33}(k_{||}, \omega)$ utilizes phase matched $(k_{||}, \omega)$ solutions of the elastic wave equation for each of the layers and of the outgoing solutions for the substrate. The amplitudes of these partial waves are related by the boundary conditions (continuity of displacement field and traction forces). For scattering from the upper surface, this yields$^{22}$

$$G_{33}(k_{||}, \omega; z = 0) = \frac{i}{\omega \text{det}(B)} \sum_n \text{adj}(B)_3^{(n)} U_3^{(n)},$$

where $B$ is the boundary condition matrix, $U$ is the polarization vector of the waves, and the sum is over the partial waves for the upper layer. Various other models can be considered, such as scattering from one of the interfaces or a certain amount of elasto-optic scattering, which modifies the terms in the sum in Eq. (2). The most striking features of the SBS spectrum are, however, determined by the zeros of $\text{det}(B)$. While the intensities of the Brillouin lines are influenced by the specific nature and location of the scattering, and also by optical interference effects, their frequencies are not. On this rationale, in our determination of the elastic constants of the layers, software we have available was used for calculating $G_{33}(k_{||}, \omega)$, fitting spectral frequencies but not for determining the complete line intensities.

As examples of calculated dispersion relations, gray scale $\text{Im} G_{33}(k_{||}, \omega)$ images for the acoustically slower material layers on a faster Si (001) substrate are presented below using elastic constants determined in this study. In these cases, all modes with phase velocities $V = \omega/k_{||}$ less than the transverse bulk wave threshold of Si (001) of 5726 m/s, namely, the Rayleigh and Sezawa modes, are true guided modes, falling off exponentially in the substrate. To render these infinitesimally narrow lines visible, a certain amount of damping must be incorporated in the calculations. Above the $T$ threshold, all modes are damped through their coupling to bulk $T$ waves of the substrate, and the damping is further increased above the $L$ threshold. A heavily damped organ pipe resonance,$^{24}$ which tends to a constant frequency as $k_{||} \to 0$, is also evident in the high-$k$ films and is discussed in more detail later.

B. Materials overview

The multilayer low-$k$ structures had the following layer sequence: The bottom most layer consisted of a 100 nm
amorphous layer of chemical vapor deposited (CVD) SiO2 (mass density = 2.25 g/cm^3) deposited on a Si (001) substrate followed by the low-κ SiOC:H interlayer dielectric (ILD) deposited via plasma-enhanced CVD (PECVD). After deposition, the low-κ ILD received an industry standard UV cure and had a final thickness of 165 nm and κ, mass density, and porosity of 2.6, 1.1 g/cm^3, and 8%–12%, respectively.12 To assess the impact of a hard mask layer on the mechanical properties of a low-κ ILD, one SiOC:H/SiO2 film stack was additionally coated with a 25 nm thick physical vapor deposited (PVD) TiN film. In this case, the thickness of the low-κ film was 150 nm, and the TiN layer had a 1:1 Ti:N ratio with 6% hydrogen and a mass density of 4.3 g/cm^3.25

The HfO2 film investigated in this study was deposited on a Si (001) substrate by atomic layer deposition (ALD) using previously described methods.26 The HfO2 film was 24.3 nm thick with k = 25 and a mass density of 9.8 g/cm^3.26 The amorphous hydrogenated boron nitride (a-BN:H) was deposited by PECVD on a Si (001) wafer using methods that have also been previously described.17 The a-BN:H film was 100 nm thick with k = 4.2 and a mass density of 1.7 g/cm^3.18

The thicknesses of the various CVD and PECVD films were determined via spectroscopic ellipsometry methods,27 while the thickness and mass density of the ALD HfO2 films were determined by X-ray reflectometry methods.28 The elemental composition and mass density of the different films were determined by combined Rutherford backscattering and nuclear reaction analysis methods described in detail elsewhere.29

III. RESULTS

A. Low-κ structures

Representative SBS spectra from a 165 nm thick blanket SiOC:H film deposited on a 100 nm thick SiO2 layer grown on a Si substrate are shown in Fig. 1(a). The spectra, recorded at angles of incidence θ ranging between 10° and 50°, reveal up to five modes for the backscattering configurations used in this study. Similarly, Fig. 1(b) shows the low frequency spectra from the 150 nm SiOC:H film with a 25 nm TiN cap layer. A strong low frequency Rayleigh-type mode emerges for θ > 50° in Fig. 1(b)—a prominent spectral feature different from the spectra recorded from the blanket film (Fig. 1(a)).

Figures 2 and 3 summarize the observed mode frequencies as a function of θ for the structures without and with the TiN cap layer, respectively. These measured (solid dark circles) and calculated (small dots) low frequency (<20 GHz) modes confirm the dispersive nature of several modes. Localized modes that are primarily associated with the 25 nm thick hard TiN layer are well separated (>150 GHz) from the low lying modes shown in Fig. 1 of the porous SiOC:H film and are not observed in SBS measurements. In addition to the simulated dispersions, the amplitude profiles of specific modes are shown in Figs. 2 and 3. These profiles emphasize the relative modal amplitude localized in each layer as shown by the components parallel (u_∥) and perpendicular (u_⊥) to the film surface. For low θ (<10°), longitudinal and transverse standing modes (LSM and TSM) have nodes or anti-nodes that are determined by the boundary conditions at the film interface.24

B. High-κ structures

Figure 4 shows several SBS spectra recorded from a 24.3 nm thick, Si-supported HfO2 film for 20° < θ < 70°. A strong Rayleigh-type mode and a broad shoulder that splits into two separated peaks at larger angles are observed. The broad mode that is composed of two modal branches appears to cross and interact most strongly for incident angles θ between 30° (k_θd = 0.27) and 40° (k_θd = 0.37), as reflected in the experimental data (Fig. 4) and confirmed in the simulated dispersions evident in the projected local density of states as illustrated (Fig. 5). At higher angles, the modes separate as evident by the dispersion for θ ~ 70° (k_θd ~ 0.54).

Spectra recorded from the 100 nm thick a-BN:H film are provided in Fig. 6. Multiple low frequency modes associated

FIG. 2. Angular dependence (θ) of frequency modes for blanket 165 nm SiOC:H/100 nm SiO2 film. The SBS data are presented as thick solid dots while the calculated fit as small dots. Modal amplitudes are included on the left where u_∥ (solid) and u_⊥ (dashed) curves represent the TSM and LSM, respectively. An additional modal amplitude is included in the top right to illustrate the sensitivity on the elastic properties of the SiO2 layer of the mode labeled as *.

FIG. 3. Angular dependence (θ) of frequency modes for 25 nm TiN/150 nm SiOC:H/100 nm SiO2 film. The SBS data are presented as thick solid dots while the calculated fit as small dots. Modal amplitudes are included on the left where u_∥ (solid) and u_⊥ (dashed) curves represent the TSM and LSM, respectively. Two additional modal amplitudes (labeled (a) and (b)) are included in the top right to illustrate the sensitivity on the elastic properties of the SiO2 layer of the modes labeled as *.

REFERENCES
with the film are observed; the variation of these mode frequencies with \( \frac{k}{d} \) is summarized in Fig. 7. At low \( \theta \), the modes are dispersive and steadily emerge with increasing frequency and spectral strength that generally rises as \( \theta \) increases towards 50°. For the relative acoustic impedances of the film compared to the Si substrate, the LSMs and TSMs for the 100 nm thick \( a \)-BN:H film are expected to be broadened as evident in the two-dimensional gray image of the projected local density of states of the excitations shown in Fig. 7 as a function of the in-plane wave vector \( k// \). The darkness of the image varies directly as the phonon density of states associated with the Green’s function component that partly determines the SBS cross section associated with the surface ripple contribution via \( u_z \), the displacements perpendicular to the film.

IV. DISCUSSION

A. Low-\( k \) SiOCH:TiN structures

The spectra illustrated in Fig. 1 can be broadly classified into two regimes—those recorded at low angles of incidence (\( \theta < 15^\circ \)) and spectra at higher \( \theta \). In the former and for the back-scattering geometry adopted, the mode wave vector \( k_z \) perpendicular to the film surface is greater than the in-plane component \( k// \); i.e., \( k_z > k// \). In these low \( \theta \) spectra, the modes are mainly composed of a series of distinct standing wave type excitations that, similar to harmonics of an organ pipe, occur due to boundary conditions at the surfaces sandwiching the given layer.24 Thus, for the SiOC:H film, different boundary conditions are in effect with and without the hard TiN over-layer. A maximum modal displacement occurs at the free SiOC:H surface and a node at the SiO2 layer interface. Such confined LSM and TSM standing modes of order \( n \) (i.e., \( n\text{LSM} \) and \( n\text{TSM} \)) for \( \theta = 0^\circ \) shown as insets in...
Fig. 2 have frequencies given by \( f_n = (2n-1)\frac{V}{2L} \) (\( n = 1, 2, 3, \ldots \)), where \( V = \sqrt{\frac{E}{\rho}} \) is the longitudinal (\( C_{11} = C_{111} \)) or transverse (\( C_{44} = C_{44} \)) mode velocity. When \( \theta \) is tuned away from normal incidence (i.e., \( \theta > 0^\circ \)), finite \( k_y \) effects come into play and the modes become dispersive (Figs. 2 and 3) where the LSMs are most sensitive to \( C_{11} \) while the TSM modes are mainly determined by \( C_{44} \). The SBS mode intensities are governed mainly by the surface ripple. Thus, the longitudinal modes are expected to dictate the low \( \theta \) spectra. Furthermore, the amplitude profiles (Fig. 2) and calculated mode dispersions confirm the observation of overlapping 2LSM (11.2 GHz) and 3TSM (10 GHz) modes for the blanket SiOC:H film. The polarization (\( u_x, u_z \) displacements) and related peak intensities are reflected in the calculated (not shown) relative SBS peak strengths associated with the measured spectrum at 10\(^6\); the 3LSM is evident at 18.9 GHz. Similarly, due to the modified boundary conditions with the presence of the TiN cap layer, the 1LSM/2TSM mode is now evident at \( \sim 8 \text{ GHz} \) (Figs. 1b and 3).

In contrast, for the low-\( \kappa \) SiOC:H film with the TiN layer (Fig. 1b)), the low frequency SBS modes associated with the SiOC:H film are defined by nodes at both top (due to TiN cap layer) and bottom interfaces (inserts Fig. 3). In this case, the organ pipe analysis requires the resonant frequencies to be \( f_n = \frac{nV}{2L} \) (\( n = 1, 2, 3, \ldots \)). Similar to the blanket SiOC:H film on SiO\(_2\)/Si, the amplitude profiles reveal a weak component penetrating into the SiO\(_2\), with extension also into the TiN cap layer. The longitudinal modes again dominate at low \( \theta \) where the overlapping 1LSM (7.4 GHz) and 2TSM (8.1 GHz) as well as a 2LSM at 13.9 GHz are observed. This doublet (\( \theta = 10^\circ \), Fig. 3) is confirmed by calculated intensity profiles from the ripple mechanism. In addition, the 1LSM/2TSM pair of modes at \( \theta = 10^\circ \) was used for determining the elastic constants of the SiOC:H layers with the TiN cap, where the stronger of the doublet pair is controlled by \( C_{111} \) of SiOC:H while the weaker peak by \( C_{44} \). Resonance frequencies recorded over \( 0^\circ < \theta < 10^\circ \) yielded the \( C_{ij} \)'s of the low-\( \kappa \) SiOC:H layers to a high accuracy (\( C_{111} = 4.7 \pm 0.2 \text{ GPa} \); \( C_{44} = 1.6 \pm 0.2 \text{ GPa} \); \( \nu = 0.24 \pm 0.05 \); \( E = 3.9 \pm 0.4 \text{ GPa} \)) as summarized in Table I in comparison to the corresponding values without the TiN cap layer.

For \( \theta > 10^\circ \), the 1LSM merges and couples to a dispersive Sezawa mode yielding the doublet observed at \( \theta = 40–60^\circ \); these particular resonances are not very sensitive to the TiN layer as the Sezawa modes extend much deeper than surface Rayleigh modes. The SiO\(_2\) layer in both structures (with and without TiN) has a relatively minor influence on the overall modal dispersion with the exception of a few modes (highlighted by * and amplitude inserts in Figs. 2 and 3). The open-closed end organ pipe type modes are still evident (Fig. 3) in the SiOC:H with only a small (<1%) fraction leaking into the SiO\(_2\) layer for \( \theta < 10^\circ \). Significant amplitude (top right insert) for \( \theta = 50^\circ \), 60\(^\circ \) is evident in the SiO\(_2\) layer for one of the observed modes. This behavior, also evident in the TiN multilayer film (inserts (a), (b) Fig. 3), confirms deeper mode penetration into the SiO\(_2\) layer for the higher frequency mode (branch (b)) than for the lower branch (a).

The strong SBS peaks (\( \theta = 50^\circ \) and 60\(^\circ \) spectra Fig. 1(b)) pertaining to the lowest branch in Fig. 3 are the Rayleigh mode. Its amplitude decreases exponentially with film depth and extends from the TiN into the SiOC:H layer. The surface ripple and attenuation of the incident light near the surface give rise to the strong Rayleigh peak. Due to the relatively high elastic constants of the TiN layer (~200 GPa compared to ~5 GPa for SiOC:H) and its small thickness (25 nm vs 150 nm SiOC:H layer), standing mode resonances associated with the TiN layer are well separated (>150 GHz) from modes linked to the porous layer (Fig. 1). Thus, there is little coupling between the low order resonances from these two distinct layers. Moreover, in agreement with the calculated SBS intensity profiles, the high frequency TiN modes are weak and not observed. While the principal elastic constants of the SiOC:H layer are determined from the low frequency resonances recorded at \( \theta < 15^\circ \), the dispersive Rayleigh mode together with the modes \( \sim 6–10 \text{ GHz} \) recorded at \( \theta > 50^\circ \) enables the \( C_{ij} \)'s of the TiN layer to be determined. The sensitivity of the low-lying Rayleigh mode to \( C_{44} \) and \( C_{111} \) of TiN follows from contributions of the longitudinal and transverse components of the mode displacements that occur, as the wave vector is tuned between \( 0^\circ < \theta < 60^\circ \).

Table I summarizes the elastic constants for the amorphous 25 nm TiN layer as determined from the dispersion and intensity plots; comparisons to other reported values for cubic TiN are also provided. The Young’s modulus for the TiN layer deduced from the present SBS study agrees closely with findings based on contact-resonance atomic force microscopy (CR-AFM)\(^{25}\) in which the TiN (16–17 nm) was grown and processed under conditions similar to the film structures investigated in this study. These amorphous TiN films have a lower density of \( \rho = 4.3 \text{ g/cm}^3 \) compared to single crystalline TiN (\( \rho = 5.4 \text{ g/cm}^3 \)). The reduction in TiN density results from the presence of hydrogen (6% of film composition) disrupting the Ti-N network bonding, leading to the decreased elastic properties compared to cubic single crystal TiN (Table II). The elastic constants and moduli of the TiN layers also depend on growth conditions such as the ratio of gases,\(^{30}\) bias potential,\(^{31,32}\) temperature,\(^{33}\) defects,\(^{34}\) and substrate material.\(^{35}\) In addition, compositional variations, particularly the evolution of an interfacial TiO layer during sputter deposition\(^{35}\) or variations in nitrogen content, can affect the mechanical properties of thinner films.\(^{36–39}\)

Concerning the mechanical properties of the low-\( \kappa \) SiOC:H film, slightly different values were obtained from the SBS measurements with and without the TiN cap layer. A least squares statistical analysis of the possible variations in this analysis indicates that the differences are significant and not within the experimental error of the measurements.
This suggests that the addition of the TiN cap layer somehow affects the mechanical properties of the low-\(k\) SiOC:H material. Such behavior is not unusual for low-\(k\) materials which are well known to be extremely sensitive to and damaged by the various plasma based processes utilized to pattern and form metal interconnect structures in these materials.\(^{46}\) This sensitivity plasma processing has been shown to result in the propensity for plasmas to remove terminal organic (CH\(_3\)) groups from the low-\(k\) material that further weakens and makes the material susceptible to further modification in downstream processing.\(^{41}\) In this regard, we postulate that the PVD TiN may have had a similar effect on the low-\(k\) SiOC:H materials investigated here. This is supported by the slight reduction in thickness from 165 to 150 nm for the low-\(k\) SiOC:H layer with the addition of the TiN cap.

### B. High-\(k\) HfO\(_2\) film

In the case of a very thin, supported layer with a lower acoustic velocity than the substrate, the Rayleigh wave dominates the SBS spectrum—a condition applicable to the 24.3 nm HfO\(_2\) film presented in this study. In addition, mismatches in the acoustic impedance (\(z = \rho v = \sqrt{\rho C_{11}}\)) between the film (\(z_f\)) and substrate (\(z_s\)) strongly affect the lifetime of modes confined within the film. Strong organ pipe resonances which appear for materials with a large mismatch, but conversely, are damped out for the case when \(z_f \sim z_s\). In the case of HfO\(_2\), the mismatch is not large enough to suppress damping and allow for detection of organ pipe modes. This broadening of the resonances is consistent with the absence of such modes in the SBS spectra (Fig. 4) and reproduced in the calculated mode densities (top inset Fig. 5), thus require other spectral characteristics to deduce all independent elastic constants of the HfO\(_2\) film by light scattering approaches.

The Rayleigh excitation decays from the HfO\(_2\) layer into the substrate and thus is controlled by both the HfO\(_2\) layer and Si. With the addition of an HfO\(_2\) layer to the silicon substrate, a Sezawa mode (branch C) controlled largely by \(C_{44}\) of the film and \(C_{11}\) of the substrate emerges starting as a broad resonance or pseudo-Sezawa mode above the T threshold of the substrate, and then becoming a true Sezawa guided mode as it dips below the T threshold of \(k_f d = 0.33\). In addition, as reflected in the dispersion and evidenced mode broadening for \(30^\circ < \theta < 40^\circ\) (0.27 < \(k_f d < 0.37\)) (Fig. 4), this mode emerges beyond the cross-over as a single peak, for example, at \(\theta = 70^\circ\) (\(k_f d = 0.54\)). This dependence on the HfO\(_2\) elastic properties enabled its \(C_{44}\) to be determined with an accuracy of \(\pm 7\%\). The other principal elastic constant, \(C_{11}\), of the high-\(k\) HfO\(_2\) film was then calculated by fitting the rest of the dispersion by fixing the film \(C_{44}\) and the known elastic constants of Si. The highest frequency (branch A) shown in Fig. 5 is most sensitive to the \(C_{11}\) elastic constant of Si. Branch B is sensitive to \(C_{44}\) of Si that couples and crosses branch C.

The phase velocity as a function of \(k_f d\) shows the Rayleigh mode, lying completely below the T threshold and is thus a true guided mode broadened by experimental effects (Fig. 8). An undamped Sezawa (branch C Fig. 5) mode emerges for \(k_f d \gtrsim 0.33\) (\(\theta \geq 35^\circ\)). Due to its interaction with the T mode of silicon (branch B in Fig. 5), this mode is damped above the T threshold. As evident in Fig. 4 by its broadening at 40\(^\circ\), the mode splits into the T Si mode and Sezawa mode as \(\theta\) increases, eventually becoming a single peak at \(\theta = 70^\circ\) (\(k_f d = 0.54\)).

Table III summarizes the elastic constants deduced for the ALD HfO\(_2\) film investigated in this study compared to those reported for other HfO\(_2\) materials grown or deposited by similar or other methods.\(^{16,42-45}\) As expected, the elastic constants and Young’s modulus deduced for the amorphous ALD HfO\(_2\) film in this study are substantially less than those reported for some single or poly-crystalline HfO\(_2\).\(^{42,45}\) However, the Young’s modulus of 166 GPa determined for the ALD film here is comparable to the values of 152 ± 13 and 220 ± 40 GPa determined by nanoindentation measurements reported by Venkatachalam\(^{16}\) and Tapily,\(^{44}\) respectively, for sputter deposited and ALD a-HfO\(_2\) films.

### C. High-\(k\) a-BN:H film

Boron nitride exists in a variety of phases including but not limited to cubic, hexagonal, amorphous hydrogenated (a-BN:H, present study) BN, and even monolayer hexagonal-BN (so named “white graphene”) giving way to a large range of mechanical properties (Table IV). A vast array of studies

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**TABLE II. Summary of results for TiN cap layer and comparisons with previous studies.**

<table>
<thead>
<tr>
<th>Group</th>
<th>(d) (nm)</th>
<th>(\rho) (g/cm(^3))</th>
<th>(C_{11}) (GPa)</th>
<th>(C_{44}) (GPa)</th>
<th>(\nu)</th>
<th>(E) (GPa)</th>
<th>Exp. method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study</td>
<td>25</td>
<td>4.3</td>
<td>230 ± 40</td>
<td>65 ± 10</td>
<td>0.3 ± 0.06</td>
<td>169 ± 21</td>
<td>SBS</td>
</tr>
<tr>
<td>Stan et al.(^{46})</td>
<td>16–17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CR-AFM</td>
</tr>
<tr>
<td>Pang et al.(^{45})</td>
<td>0–4180</td>
<td>5.4</td>
<td>285–475</td>
<td>107–179</td>
<td>0.2</td>
<td>446(^{6})</td>
<td>AM</td>
</tr>
<tr>
<td>Kim et al.(^{46})</td>
<td>100–2800</td>
<td>5.39</td>
<td>625</td>
<td>163</td>
<td>0.194</td>
<td>416(^{6})</td>
<td>PR</td>
</tr>
<tr>
<td>Meng et al.(^{47})</td>
<td>225</td>
<td>5.46</td>
<td>507</td>
<td>163</td>
<td>0.2</td>
<td>200–600</td>
<td>NI</td>
</tr>
<tr>
<td>Jiang et al.(^{38})</td>
<td>300–900</td>
<td>~3.5–5.4(^{46})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NI</td>
</tr>
<tr>
<td>Schneider et al.(^{48})</td>
<td>800–3500</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PLU</td>
</tr>
<tr>
<td>Vijgen et al.(^{49})</td>
<td>1650</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NI</td>
</tr>
<tr>
<td>Abadías et al.(^{50})</td>
<td>360</td>
<td>5.15</td>
<td>387</td>
<td>130</td>
<td></td>
<td></td>
<td>PLU/SBS</td>
</tr>
</tbody>
</table>

\(^{a}\)Anisotropic (110).

\(^{b}\)Densities estimated from Ref. 51
have been performed over the years to study the properties of these BN phases, some of which are presented in Table IV. Our measured values are in agreement with Ref. 18 in which similar materials and processing were used. Comparisons to other studies of h-BN reveal that our measured values of elastic constants and Young’s modulus are lower. This may be attributed to the lowered density and the presence of hydrogen in the film of the present study. Finally, a few studies that highlight the elastic properties of c-BN are provided (Table IV) with values much larger than those of h-BN, as the cubic phase is harder than the hexagonal phase. The dispersive low

TABLE III. Summary of results for HfO$_2$ film and comparison with previous studies. d: film thickness, $\rho$: film density, $\nu$: Poisson’s ratio, E: Young’s modulus, NI: nano indentation, SR: sonic resonance.

<table>
<thead>
<tr>
<th>Group</th>
<th>d (nm)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$c_{11}$ (GPa)</th>
<th>$c_{44}$ (GPa)</th>
<th>$\nu$</th>
<th>E (GPa)</th>
<th>Exp. method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study</td>
<td>24.3</td>
<td>9.8</td>
<td>280 $\pm$ 30</td>
<td>61 $\pm$ 4</td>
<td>0.36 $\pm$ 0.02</td>
<td>166 $\pm$ 10</td>
<td>SBS</td>
</tr>
<tr>
<td>Shan et al.$^{32}$</td>
<td></td>
<td>$\quad$</td>
<td>561</td>
<td>111</td>
<td></td>
<td></td>
<td>theory</td>
</tr>
<tr>
<td>Tkachev et al.$^{34}$</td>
<td>405</td>
<td>10.1</td>
<td>$\quad$</td>
<td>187</td>
<td></td>
<td></td>
<td>SBS</td>
</tr>
<tr>
<td>Tapily et al.$^{44}$</td>
<td>60</td>
<td>$\quad$</td>
<td>$\quad$</td>
<td>$\quad$</td>
<td>220 $\pm$ 40</td>
<td></td>
<td>NI</td>
</tr>
<tr>
<td>Venkatachalam et al.$^{16}$</td>
<td>154</td>
<td>9.68</td>
<td>$\quad$</td>
<td>$\quad$</td>
<td>152 $\pm$ 13$^a$</td>
<td>166 $\pm$ 8$^b$</td>
<td>NI</td>
</tr>
<tr>
<td>Dole et al.$^{45}$</td>
<td></td>
<td>$\quad$</td>
<td>$\quad$</td>
<td>$\quad$</td>
<td>0.22--0.3</td>
<td>100--240</td>
<td>SR</td>
</tr>
</tbody>
</table>

$^a$Amorphous.
$^b$Polycrystalline.

TABLE IV. Summary of results for a-BN:H film and comparison with previous studies. d: film thickness, $\rho$: film density, $\nu$: Poisson’s ratio, E: Young’s modulus, NI: nano indentation.

<table>
<thead>
<tr>
<th>Group</th>
<th>d (nm)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$c_{11}$ (GPa)</th>
<th>$c_{44}$ (GPa)</th>
<th>$\nu$</th>
<th>E (GPa)</th>
<th>Exp. method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study</td>
<td>100</td>
<td>1.7</td>
<td>52 $\pm$ 6</td>
<td>19 $\pm$ 2</td>
<td>0.21 $\pm$ 0.07</td>
<td>46 $\pm$ 8</td>
<td>SBS</td>
</tr>
<tr>
<td>King et al.$^{8,a}$</td>
<td></td>
<td>1.9</td>
<td>$\quad$</td>
<td>$\quad$</td>
<td>47 $\pm$ 5</td>
<td></td>
<td>NI</td>
</tr>
<tr>
<td>Wittkowski et al.$^{52,b}$</td>
<td>25--610</td>
<td>2.14</td>
<td>65</td>
<td>53</td>
<td>90.5</td>
<td></td>
<td>SBS</td>
</tr>
<tr>
<td>Wittkowski et al.$^{53,e}$</td>
<td>123, 277</td>
<td>3.3</td>
<td>$\quad$</td>
<td>226</td>
<td>$\quad$</td>
<td></td>
<td>SBS</td>
</tr>
<tr>
<td>Grimsditch et al.$^{54,c,d}$</td>
<td>3.48</td>
<td>820</td>
<td>$\quad$</td>
<td>$\quad$</td>
<td>$\quad$</td>
<td></td>
<td>SBS</td>
</tr>
</tbody>
</table>

$^a$a-BN:H.
$^b$Hexagonal BN.
$^c$cubic BN.
$^d$Single crystal.
frequency modes of the supported α-BN:H films (Fig. 6) and their Brillouin peak intensities are accounted for by the projected density of states as shown in Fig. 7. By fitting these modes to the dispersion, the individual elastic constants $C_{44} = 52 \pm 6$ GPa and $C_{14} = 19 \pm 2$ GPa were deduced.

Similar to the case of HfO$_2$, low angle organ pipe resonances for BN:H were not observed due to modal damping. Therefore, the elastic constants once again were determined from the observed behavior of the undamped higher frequency Rayleigh and Sezawa modes. The Rayleigh mode from the a-BN:H film (lowest mode Figs. 7 and 9) lies completely below the T threshold (Fig. 9) while a Sezawa mode emerges below the T threshold for 35$^\circ$ and 9$^\circ$ lies completely below the T threshold (Fig. 9) while a true Sezawa mode with intensity comparable to the Rayleigh mode at $\theta = 45^\circ$. With $C_{44}$ determined, $C_{11}$ was deduced by its effect on the frequency of the Rayleigh mode.

V. SUMMARY

In conclusion, we have investigated the elastic constants of several low-$k$ and high-$k$ dielectric thin films. In addition to blanket SiOC:H layers, the role of a thin 25 nm TiN cap film modes was studied. By probing the dispersion of LSM and TSM-type excitations and comparison to the projected local density of phonon states, the TiN layers are found to influence the principal elastic constants of the porous SiOC:H film. Despite a lack of spectral evidence of discrete acoustic resonances associated with the TiN layer, the sensitivity of other features in the SBS spectra to the properties of TiN allowed for the mechanical properties of the cap layer to be deduced.

The mechanical properties of two high-$k$ films, HfO$_2$ and α-BN:H, were also investigated. Due to the acoustic mismatch between the individual films and the substrate, the high frequency standing wave modes are damped—especially those originating from HfO$_2$. The dependence of particular dispersive low frequency Brillouin modes enabled the mechanical properties of the two high-$k$ films to be evaluated.