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Elastic properties of porous low-k dielectric nano-films

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Low-k dielectrics have predominantly replaced silicon dioxide as the interlayer dielectric for interconnects in state of the art integrated circuits. In order to further reduce interconnect RC delays, additional reductions in k for these low-k materials are being pursued via the introduction of controlled levels of porosity. The main challenge for such dielectrics is the substantial reduction in elastic properties that accompanies the increased pore volume. We report on Brillouin light scattering measurements used to determine the elastic properties of these films at thicknesses well below 200 nm, which are pertinent to their introduction into present ultralarge scale integrated technology. The observation of longitudinal and transverse standing wave acoustic resonances and their transformation into traveling waves with finite in-plane wave vectors provides for a direct non-destructive measure of the principal elastic constants that characterize the elastic properties of these porous nano-scale films. The mode dispersion further confirms that for porosity levels of up to 25%, the reduction in the dielectric constant does not result in severe degradation in the Young’s modulus and Poisson’s ratio of the films. © 2011 American Institute of Physics. [doi:10.1063/1.3624583]

I. INTRODUCTION

As the semiconductor industry strives to keep pace and sustain Moore’s law, new materials are increasingly being introduced into micro-/nano-electronic products. Among these material innovations are dielectric materials with a dielectric constant (k) less than or greater than that of SiO2—so called low-k and high-k dielectrics. Both low- and high-k dielectrics are currently utilized in the high volume manufacturing of transistors and interconnect structures for advanced microprocessors. For example, a low-k SiOC:H interlayer dielectric (ILD) has been introduced at the 90 nm interconnect technology node,1 and a high-k Hf based gate dielectric has been introduced at the 45 nm transistor technology node.2 As stated in the 2009 International Technology Roadmap for Semiconductors,3,4 dielectric materials with still higher and lower dielectric constants will be needed for future 22 and 16 nm technologies.

For low-k dielectrics, the principle means for reducing the dielectric constant has been the introduction of various organic constituents into a SiO2 matrix to make a carbon doped oxide (CDO) or SiOC:H material. The organic component in the SiOC:H material is typically present in the form of terminal methyl (CH3) groups, which disrupt the connectedness of the SiO2 network and result in a lower density material.5 The lower density leads to a lower dielectric constant due to the reduced electronic and ionic contributions to the dielectric function of the material.6,7 However, the lower density achieved through decreased network inter-connectedness also leads to reduced mechanical properties such as Young’s modulus, hardness, and fracture toughness.8–11 Low-k dielectric materials also exhibit intrinsic tensile stresses and increased coefficients of thermal expansion relative to SiO2.5,9 For these reasons, thin film cracking and adhesion are serious thermal-mechanical reliability issues for low-k dielectric materials.12,13 Unfortunately, the required continued reduction in the dielectric constant will require decreases in density that will eventually lead to the formation of various levels of nano-porosity inside the low-k dielectric. Porous low-k dielectrics (PLKs) are expected to have mechanical properties that are still further reduced relative to those of their non-porous counterparts, as well as increased reliability concerns due to the presence of porosity.14–16 For these reasons, accurate measurements of properties such as the elastic constant C0, Young’s modulus, and Poisson’s ratio are needed for PLK materials.

The most common method for measuring Young’s modulus of a thin film is nano-indentation.17 This technique, however, typically requires relatively thick films (1 to 2 microns) in order to avoid substrate-indenter interactions.18 As the semiconductor industry moves to 22 nm technologies and beyond, the low-k ILD thickness in interconnects will approach 100 nm or less, and the suitability of nano-indentation techniques on porous materials is not apparent. Therefore, non-destructive techniques capable of measuring the elastic constants of materials of thickness ≤150 nm are needed. Further, the thermal mechanical modeling of low-k interconnects also requires knowledge of Poisson’s ratio. Poisson’s ratio is typically assumed to be 0.25 to 0.33 for most dielectric materials. However, the value of Poisson’s ratio for a nano-porous dielectric material is not intuitively obvious and has been assumed to be anywhere from 0 to 0.2.19,20 Negative values have also been reported for some porous “auxetic” materials.21 Therefore, an accurate determination of Poisson’s ratio for PLKs of interest to the semiconductor industry is needed.

In this paper, we report on Brillouin light scattering (BLS) measurements of PLKs. We draw upon our previous

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successes\textsuperscript{22} in applying BLS to non-porous low-k dielectrics to determine the elastic constants of select PLKs. The thin films are taken to be elastically isotropic, implying that the material can be described by two principal elastic constants. The isotropy of the films was also evident when no particular in-plane symmetry was observed in the acoustic mode dispersions as determined by our BLS measurements when the sample was rotated in the film plane through small discrete angles. For these porous low-k dielectric thin film materials, isotropic behavior is a legitimate assumption,\textsuperscript{23} allowing the Young’s modulus, $E = \left[ (1 + \nu) \left(1 - 2\nu\right) C_{12}\right]/\nu$, and Poisson’s ratio, $\nu = C_{12}/\left(\left(1 + C_{11} - 2C_{44}\right)\right)$, to be calculated from the $C_{11}$ and $C_{44}$ elastic constants which, as discussed later, are especially sensitive to the longitudinal- (LSM) and transverse-standing mode (TSM) frequencies, which are non-destructively measured by BLS and scale as $\sqrt{C_{11}}$ (LSM) and $\sqrt{C_{44}}$ (TSM).

II. EXPERIMENT

All thin film materials investigated in this study were deposited on (001) silicon wafers via plasma enhanced chemical vapor deposition (PECVD) using various combinations of silane, organosilanes, hydrogen, helium, oxidizers, and porogens.\textsuperscript{12} Deposition temperatures were on the order of 250 °C to 400 °C. Some films received a post deposition e-beam or UV cure in order to enhance the network connectivity and mechanical properties.\textsuperscript{24} The film thicknesses ($h$) ranged between 100 and 200 nm and densities from 1.10 to 1.35 g/cm$^3$. Table I summarizes the general process conditions used to deposit the films in this study and in our previous study.\textsuperscript{25}

Table II summarizes some of the general material properties for the films in this study, including the nominal film thickness ($h$), dielectric constant ($k$), refractive index ($n$), mass density ($\rho$), porosity, pore diameter, and film composition. The film thickness and refractive index were measured using a J. A. Woollam variable angle spectroscopic ellipsometer. The film thickness and refractive index were measured with the Variable Angle Spectroscopic Ellipsometry (VASE) time-of-flight system.\textsuperscript{26}

The BLS measurements were performed in a backscattering geometry at room temperature with a tandem Fabry-Perot interferometer operated in a sequential six-pass configuration.\textsuperscript{27} Approximately 70 mW of p-polarized $\lambda_0 = 514.5$ nm laser radiation focused to a spot diameter of 35 to 50 μm was used to record the unpolarized ($p + s$) spectra; a typical measurement time for each spectrum ranged from 0.5 to 2 h. The BLS laser peak power per unit area was approximately six orders of magnitude less than the corresponding value in the

<table>
<thead>
<tr>
<th>Sample #</th>
<th>h (nm)</th>
<th>k</th>
<th>n</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>Porosity (%)</th>
<th>Pore diameter (A)</th>
<th>XPS composition (% Si, C, O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$<em>{1.8}$C$</em>{0.2}$H#1</td>
<td>100</td>
<td>3.20</td>
<td>1.678</td>
<td>1.15</td>
<td>&lt;2</td>
<td>ND</td>
<td>15.7%, 77.8%, 6.7%</td>
</tr>
<tr>
<td>Si$<em>{1.8}$C$</em>{0.2}$H#2</td>
<td>100</td>
<td>3.20</td>
<td>1.679</td>
<td>1.15</td>
<td>&lt;2</td>
<td>ND</td>
<td>15.2%, 77.9%, 7.1%</td>
</tr>
<tr>
<td>Si$<em>{1.8}$C$</em>{0.2}$H#3</td>
<td>200</td>
<td>2.85</td>
<td>1.584</td>
<td>1.15</td>
<td>8 to 12</td>
<td>4 to 6</td>
<td>14.7%, 78.2%, 7.2%</td>
</tr>
<tr>
<td>SiOC:H#1</td>
<td>100</td>
<td>2.55</td>
<td>1.558</td>
<td>1.10</td>
<td>&lt;2</td>
<td>ND</td>
<td>33%, 46%, 21%</td>
</tr>
<tr>
<td>SiOC:H#2</td>
<td>100</td>
<td>2.60</td>
<td>1.482</td>
<td>1.10</td>
<td>8 to 12</td>
<td>&lt;10</td>
<td>34%, 52%, 14%</td>
</tr>
<tr>
<td>SiOC:H#3</td>
<td>200</td>
<td>2.50</td>
<td>1.340</td>
<td>1.25</td>
<td>≤25</td>
<td>15 to 20</td>
<td>29%, 18%, 53%</td>
</tr>
<tr>
<td>SiOC:H#4</td>
<td>150</td>
<td>2.50</td>
<td>1.340</td>
<td>1.25</td>
<td>≤25</td>
<td>15 to 20</td>
<td>29%, 18%, 53%</td>
</tr>
<tr>
<td>CDO$^a$</td>
<td>100</td>
<td>3.10</td>
<td>1.430</td>
<td>1.35</td>
<td>ND</td>
<td>ND</td>
<td>33%, 29%, 39%</td>
</tr>
</tbody>
</table>

$^a$From a previous study (Ref. 22).

ND = Not detected.

Elemental film composition was determined using x-ray photoelectron spectroscopy (XPS). All XPS data were collected using a VG Theta 300 XPS system equipped with a hemispherical analyzer and a monochromated Al anode x-ray source (1486.6 eV). The emitted photoelectrons were detected using a pass energy of 20 eV for high resolution scans of the Si 2p, C 1s, and O 1s core levels. XPS depth profiling was performed using a 5 keV Ar$^+$ ion sputtering beam.\textsuperscript{12}

The mass density for all films was determined via x-ray reflectivity (XRR). The XRR spectra were collected using both a Bede Fab200 Plus (employing a Cu microbeam source and an asymmetric cut Ge crystal) and a Siemens D5000 (employing a Cu line source and graphite monochromator).\textsuperscript{26} The data were collected in the range of 0 to 9000 to 15 000 arc sec with approximately 20 arc sec steps. Spectra were acquired from 100 nm films and fitted using the $R_\text{LL}$ software package (version 4.0, Bede). The XRR spectra were fitted by adjusting the film thickness, mass density, and surface/interface roughness.

The XRR measurements were performed in a backscattering geometry at room temperature with a tandem Fabry-Perot interferometer operated in a sequential six-pass configuration.\textsuperscript{27} Approximately 70 mW of p-polarized $\lambda_0 = 514.5$ nm laser radiation focused to a spot diameter of 35 to 50 μm was used to record the unpolarized ($p + s$) spectra; a typical measurement time for each spectrum ranged from 0.5 to 2 h. The BLS laser peak power per unit area was approximately six orders of magnitude less than the corresponding value in the

Table I. Summary of general process gases and conditions utilized to deposit the low-k dielectric films in this study through PECVD. The concentrations of the constituents are indicated by p, q, and r.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Precursors/Gases</th>
<th>Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$<em>{1.8}$C$</em>{0.2}$H#1</td>
<td>H$_2$/He/H$_2$Si(C$_q$H$_r$)$_1$-p</td>
<td>No</td>
</tr>
<tr>
<td>Si$<em>{1.8}$C$</em>{0.2}$H#2</td>
<td>H$_2$/He/H$_2$Si(C$_q$H$_r$)$_1$-p</td>
<td>No</td>
</tr>
<tr>
<td>Si$<em>{1.8}$C$</em>{0.2}$H#3</td>
<td>H$_2$/He/H$_2$Si(CH$_q$)$_1$-p and Porogen</td>
<td>Ebeam</td>
</tr>
<tr>
<td>SiOC:H#1</td>
<td>H$_2$/Oxidizer/H$_2$SiOC(CH$_q$)$_1$-p</td>
<td>UV</td>
</tr>
<tr>
<td>SiOC:H#2</td>
<td>H$_2$/Oxidizer/H$_2$SiOC(CH$_q$)$_1$-p and Porogen</td>
<td>UV</td>
</tr>
<tr>
<td>SiOC:H#3</td>
<td>H$_2$/Oxidizer/H$_2$SiOC(CH$_q$)$_1$-p and Porogen</td>
<td>Ebeam</td>
</tr>
<tr>
<td>SiOC:H#4</td>
<td>H$_2$/Oxidizer/H$_2$SiOC(CH$_q$)$_1$-p and Porogen</td>
<td>Ebeam</td>
</tr>
<tr>
<td>CDO$^a$</td>
<td>H$_2$/Oxidizer/H$_2$SiOC(C$_q$H$_r$)$_1$-p</td>
<td>No</td>
</tr>
</tbody>
</table>

$^a$From a previous study (Ref. 22).

ND = Not detected.
picosecond ultrasonic measurement. The standing wave excitations with discrete wave vector components perpendicular to the film \(\mathbf{K}_\perp\) were most clearly observed at small scattering angles \(\theta\), where \(\theta\) is the deviation of the backscattered beam from the film normal \((z\text{-axis})\). Measurements were also recorded when \(\theta\) increased from \(\sim 0^\circ\) to \(60^\circ\), thereby monitoring the transformation of longitudinal and transverse standing wave modes into traveling modes with a progressively larger in-plane wave vector \(\mathbf{K}_\parallel = (4\pi/\lambda_0) \sin \theta\) along the \(x\)-direction. The velocity of the traveling modes is thus given by \(V = \lambda_0/2 \sin \theta\), where \(f\) is the measured frequency of the mode. The elastic properties of seven samples with varying compositions and degrees of porosity were investigated.

For comparison to the BLS results, Young’s modulus for these films was also determined using both nano-indentation (NI) and picosecond laser ultrasonics (PLU). The details of these measurements have been described in prior publications. Briefly, the indentation experiments were performed on 2 \(\mu\)m thick PLK films using a Hysitron Triboindenter and a Berkovich diamond tip with a load range of up to 30 mN. Samples were loaded in a partial unloading mode up to 2 mN in this study. The modulus was calculated using a shallow contact depth range below 10\% of the film thickness in order to minimize substrate interaction effects, which can be pronounced for very low-\(k\) films. However, due to the low modulus of PLK films, the interaction from the Si substrate is not necessarily completely removed. NI measures the plane strain reduced Young’s modulus \(E_r\). Young’s modulus \((E)\) is then calculated using the expression \(E = (1 - \nu^2)/E + (1 - \nu^2)/E_i\), where \(E_i\) and \(\nu_i\) are the Young’s modulus and Poisson’s ratio for the SI diamond tip. Typically, Poisson’s ratio is assumed to be 0.25 to 0.33 for NI measurements of dielectric materials. The validity of this assumption is discussed later in this article based on a comparison to Poisson’s ratio as determined from the BLS measurements.

PLU measurements were performed using an optical pump and probe technique. An ultrafast laser is utilized to expose the film surface to an optical pulse of less than a pico-second in duration. The laser light is absorbed by the thin film surface and generates a strain pulse that propagates into the bulk of the film. A portion of that strain pulse propagates down the film-substrate interface and reflects back to the surface, where it is detected using a second time-delayed “probe” laser as a change in the reflectivity of the surface. The transit time of the reflected strain pulse is proportional to the longitudinal sound velocity, from which Young’s modulus can also be computed by assuming elastic isotropy and pre-existing knowledge of the mass density and Poisson’s ratio for the film of interest.

III. RESULTS

To illustrate the main features of our study, we present spectra and analysis from two samples, one lying at the threshold of porosity \((\lesssim 2\%)\) and the other at a relatively large porosity \((25\%)\). Figure 1 displays BLS spectra as a function of the scattering angle \(\theta\) from \(0^\circ\) to \(60^\circ\) for \(\text{Si}_{0.2}\text{C}_{0.8}\text{H}\#2\) \((h = 100 \text{ nm}, \leq 2\% \text{ porosity})\). At small \(\theta\) \((\lesssim 5^\circ)\), the peaks at 5.8 GHz and 18.5 GHz are excitations with vanishing \(K_\parallel\) and are identified, respectively, as the \(N = 1\) and \(N = 2\) longitudinal standing modes \((1\text{LSM} \text{and} 2\text{LSM})\). In addition, the weak mode at 9.8 GHz occurring at \(\theta = 5^\circ\) emerges from the \(N = 2\) transverse standing mode \(2\text{TSM}\). Calculations revealed that the \(3\text{TSM}\) occurs at 16.3 GHz for \(\theta < 20^\circ\), which was not resolved in the BLS measurements. For increasing \(\theta\), the modes become dispersive and additional excitations are evident in the spectra.

Mode frequencies determined by fitting a Gaussian profile to each peak and averaging the Stokes and anti-Stokes shifted frequencies are shown in Fig. 2. Fits to the dispersion are calculated by finding resonances in the elastodynamic Green’s tensor following the method of Every et al. In the present case of a thin film supported on a substrate, this approach consists of solving the wave equation in each medium subject to the presence of a delta force acting on the free surface and the usual boundary conditions related to continuity of stress and displacement at the interface. The best fits to the data in Fig. 2 were obtained using \(C_{11} = 6.5\) GPa.
As in Fig. 2, the calculated dispersion curves for this film (Fig. 4) yield \( C_{11} < \) and the elastic properties of the PLK thin film samples evaluated. Similar spectra were measured from the other films, and the lower three lines are the corresponding modes calculated for the bulk low-k film. The mode amplitudes parallel to the propagation direction \((U_x)\) and normal \((U_z)\) to the film were calculated at low \( \theta \) \((= 5^\circ)\) and are illustrated in the left-hand panel of Fig. 2. The standing wave feature is well defined and confirms the principally longitudinal (LSM) or transverse (TSM) character of the modes.

Representative spectra from the \( h = 150 \) nm SiOC:H\#4 sample with 25\% porosity are displayed in Fig. 3. The BLS intensity associated with the longitudinal modes is generally strongest at low angles, with additional modes appearing with increasing \( \theta \). Calculations reveal distinct 1LSM and 2TSM modes at 4.5 and 8.4 GHz, respectively, and the 2LSM and 3TSM modes overlap near 14.1 GHz for \( \theta \approx 0^\circ \). As in Fig. 2, the calculated dispersion curves for this film (Fig. 4) yield \( C_{11} = 10.0 \) GPa, \( C_{12} = 2.9 \) GPa, and \( C_{44} = 3.6 \) GPa. Similar spectra were measured from the other films, and the elastic properties of the PLK thin film samples evaluated in this study are summarized in Table III.

### IV. DISCUSSION

As is evident in the mode amplitudes of Figs. 2 and 4, the acoustic excitations observed at \( \theta < 5^\circ \) \((K_t \approx 0)\) in general separate into highly polarized longitudinal or transverse excitations. Their underlying physics stems from a simple physical analog of acoustic modes associated with an organ pipe in which vibrations at the film surface and film-substrate interface are akin to those at the open and closed ends of the organ pipe.31 The LSM and TSM excitations are, respectively, most sensitive to the \( C_{11} \) and \( C_{44} \) \((C_{12})\) elastic constants of the elastically isotropic low-k films. In this case, the standing wave mode frequencies are provided by \( f = (2m + 1)\sqrt{h/V} \), where \( m \) is an integer, \( h \) is the film thickness, and \( V \approx \sqrt{c_{ij}/\rho} \) is the mode velocity. The frequency \( f \) and spacing \( \Delta f = V/2h \) between neighboring longitudinal or transverse resonances at small \( \theta \) thus provide a sensitive measure of the principal elastic constants of the film. As expected, \( C_{11} \) is mainly determined from the LSM modes at low \( \theta \) \((< 10^\circ)\). For example, in the case of the film with 25\% porosity, \( C_{11} \) spans over a relatively narrow range of \( \pm 4\% \) to yield the LSM mode frequencies within its measurement uncertainty of \( \pm 0.2 \) GHz. Likewise, the TSM branch is most sensitive to the \( C_{44} \) \((and C_{12})\) that are determined to within an accuracy of \( \pm 6\% \). The complete mode dispersion is also constrained by the known film thickness and density. The uncertainties for \( \nu \) and \( E \) were then calculated from the error margins of \( C_{11} \) and \( C_{44} \).

The deduced \( C_{ij} \) values illustrate the value of Brillouin light scattering as a viable approach for non-destructively determining the elastic constants, Young’s modulus, and Poisson’s ratio of the porous nano-films. Young’s modulus for the seven samples investigated in this study is found to range between 3.5 and 8.7 GPa. These values are consistent with NI Young’s modulus measurements reported for non-porous and porous low-k dielectric materials with similar dielectric constants. Typical reported NI values are in the range of 9–18 GPa for non-porous materials9,11,18,19,33–36 and 3.5–9 GPa for porous materials.9,19,34–38 For further comparison, the lower values of Young’s modulus are comparable to those of nylon39 (2 to 4 GPa) and polystyrene (3 to 3.5 GPa).40 As another comparison, Young’s modulus for aero-/xerogel

### TABLE III. Summary of the BLS results, where \( E \) is Young’s modulus.

<table>
<thead>
<tr>
<th>Material</th>
<th>Porosity</th>
<th>( C_{11} ) (GPa)</th>
<th>( C_{44} ) (GPa)</th>
<th>Poisson ratio</th>
<th>( E ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Si_{0.2}C_{0.8}H #3 )</td>
<td>&lt;2%</td>
<td>6.5 ± 0.3</td>
<td>1.3 ± 0.2</td>
<td>0.38 ± 0.01</td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>( Si_{0.2}C_{0.8}H #2 )</td>
<td>&lt;2%</td>
<td>6.5 ± 0.4</td>
<td>1.9 ± 0.2</td>
<td>0.30 ± 0.01</td>
<td>4.8 ± 0.7</td>
</tr>
<tr>
<td>( Si_{0.2}C_{0.8}H #1 )</td>
<td>8 to 12%</td>
<td>10.0 ± 0.3</td>
<td>2.6 ± 0.2</td>
<td>0.33 ± 0.01</td>
<td>6.8 ± 0.9</td>
</tr>
<tr>
<td>SiOC:H#1</td>
<td>&lt;2%</td>
<td>7.1 ± 0.4</td>
<td>2.4 ± 0.2</td>
<td>0.25 ± 0.01</td>
<td>5.9 ± 1.1</td>
</tr>
<tr>
<td>SiOC:H#2</td>
<td>12%</td>
<td>6.5 ± 0.2</td>
<td>2.4 ± 0.1</td>
<td>0.22 ± 0.01</td>
<td>5.7 ± 1.1</td>
</tr>
<tr>
<td>SiOC:H#3</td>
<td>25%</td>
<td>9.0 ± 0.4</td>
<td>3.5 ± 0.2</td>
<td>0.18 ± 0.01</td>
<td>8.3 ± 1.6</td>
</tr>
<tr>
<td>SiOC:H#4</td>
<td>25%</td>
<td>10.0 ± 0.4</td>
<td>3.6 ± 0.2</td>
<td>0.22 ± 0.01</td>
<td>8.7 ± 1.5</td>
</tr>
</tbody>
</table>
materials, which are extremely porous SiO₂ matrix low-k dielectrics (k < 2, ρ < 0.6 g/cm³, porosity = 50% to 90%), ranges from 0.0005 to 0.0005 GPa.\(^{41-44}\)

Within this sample set, which spans the SiO₂CₓHᵧ phase diagram for the region of 0-25% porosity, x = 0.4 to 1.8, and y = 0.6 to 5.0, there is an interesting variation in Young’s modulus. The lowest modulus film is Si₀.₂C₀.₈:H#1 with a Young’s modulus of 3.5 GPa. Interestingly, this film has a lower modulus than Si₀.₂C₀.₈:H#3, which has approximately the same composition but significant levels of porosity. The higher elastic modulus for Si₀.₂C₀.₈:H#3 is believed to be partially a result of the additional electron beam cure that this film received. Electron beam cures are well established for increasing the network connectivity of low density materials and accordingly increasing the elastic modulus of the dielectric film.\(^{45}\) The higher modulus might also be a result of using a lower carbon content organosilane that enables better Si–C network bond formation and connectivity. It should also be noted that although no oxygen containing elements were detected in this film as well as for Si₀.₂C₀.₈:H#1 & 2. The presence of oxygen is due to the low density of this film and the ability of ambient moisture to diffuse into and react with weak chemical bonds within the film.\(^{46}\) Depending on how the oxygen is incorporated, this could also result in small variations in Young’s modulus for films with similar Si/C ratios.

The highest elastic modulus films in this study are also the highest porosity films. SiOC:H#3 & 4 both have porosity levels approaching 25% with Young’s moduli of 8.3 to 8.7 GPa. In addition to receiving an electron beam cure, these films also have the highest oxygen content as determined by XPS (as well as for Si₀.₂C₀.₈:H#1 & 2). The presence of oxygen is due to the low density of this film and the ability of ambient moisture to diffuse into and react with weak chemical bonds within the film.\(^{45}\) The incorporation of small amounts of oxygen into the network structure of Si₀.₂C₀.₈:H#1-3 can have a significant stiffening effect on Young’s modulus for these materials.

Additional interesting differences between the films in this sample set are also observed for Poisson’s ratio. As is evident from Table III, ν is found to range from 0.18 to 0.38. The high value of ν = 0.38 for Si₀.₂C₀.₈:H#1 is comparable to that of typical polymeric materials such polycarbonate and polytetrafluoroethylene (Teflon) for which ν is reported to range from 0.3 to 0.4.\(^{51-53}\) In this regard, we note that dual cantilever beam measurements for Si₀.₂C₀.₈:H#3 have shown increased fracture energies that are 3 to 4 times those for other PLK materials and are consistent with those of other polymeric materials.\(^{54}\) The values of ν = 0.30 to 0.38 for Si₀.₂C₀.₈:H#1-3 therefore suggest the possibility of observing increased fracture energies of these materials.

The lowest Poisson’s ratio value of 0.18 was observed for SiOC:H#3, which has the highest porosity among the films investigated. This value is comparable to and consistent with the values of Poisson’s ratio for aerogel materials, which have been reported to be in the range of 0.15–0.26.\(^{42,43}\) For these materials, ν decreases from 0.26 for <10% porosity to ≤0.16 for >90% porosity. Aerogels with porosities of 20% to 40% typically have ν = 0.18 to 0.22,\(^{43}\) which is in excellent agreement with our results for SiOC:H#2-4. The value of ν = 0.25 for SiOC:H#1 is consistent with our previous report of 0.26 for a non-porous carbon doped oxide\(^{22}\) (k = 3.1) and the upper bound on ν observed for aerogel materials.\(^{43}\) The Poisson’s values for SiOC:H#1-4 are also consistent with two independent BLS measurements in which ν was reported to be 0.15 ± 0.02 for a non-porous SiOC:H thin film dielectric (k = 3.0, ρ = 1.5 g/cm³) (Ref. 55) and 0.26 ± 0.1 for a low porosity SiOC:H dielectric (ρ = 1.18 g/cm³, porosity = 16%).\(^{56}\) The corresponding Young’s moduli of these ~1000 nm thick films\(^{55,56}\) measured using BLS range between 7.8 and 1.4 GPa from non-porous to ~25% porosity. As noted above, the process that underlies the growth and fabrication of such low-k films can affect the elastic properties, and this could account for the differences in E reported for the various films. The maximum uncertainties in Young’s modulus determined from these BLS measurements are similar to those reported in the present study.

In Table IV, we compare the Young’s moduli determined through BLS, NI, and PLU. The NI and PLU measurements were both performed independent of the BLS results and assume a Poisson’s ratio of 0.25. As can be seen, the values from all techniques agree with one another to within ±4 GPa. For most of the films, the NI Young’s moduli are slightly higher than those determined by both BLS and PLU techniques. This is consistent with our previous

<table>
<thead>
<tr>
<th>Sample #</th>
<th>BLS-E (GPa)</th>
<th>NI-E (GPa)</th>
<th>PLU-E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₀.₂C₀.₈:H#1</td>
<td>3.5 ± 0.4</td>
<td>4.9 ± 0.2</td>
<td>4 ± 0.4</td>
</tr>
<tr>
<td>Si₀.₂C₀.₈:H#2</td>
<td>4.8 ± 0.7</td>
<td>6.3 ± 0.2</td>
<td>4 ± 0.4</td>
</tr>
<tr>
<td>Si₀.₂C₀.₈:H#3</td>
<td>6.8 ± 0.9</td>
<td>5.6 ± 0.4</td>
<td>4.3 ± 0.4</td>
</tr>
<tr>
<td>SiOC:H#1</td>
<td>5.9 ± 1.1</td>
<td>7.5 ± 0.4</td>
<td>NM</td>
</tr>
<tr>
<td>SiOC:H#2</td>
<td>5.7 ± 1.1</td>
<td>9.7 ± 0.4</td>
<td>NM</td>
</tr>
<tr>
<td>SiOC:H#3</td>
<td>8.3 ± 1.6</td>
<td>8.3 ± 0.4</td>
<td>5.9 ± 0.6</td>
</tr>
<tr>
<td>SiOC:H#4</td>
<td>8.7 ± 1.5</td>
<td>8.1 ± 0.4</td>
<td>5.9 ± 0.6</td>
</tr>
<tr>
<td>CDO*</td>
<td>8.4 ± 6.1</td>
<td>11.80</td>
<td>8.9 ± 0.9</td>
</tr>
</tbody>
</table>

*aFrom Ref. 22.

NM = Not measured. Samples burned under pump laser.

Note: The reported uncertainties for NI-E and PLU-E represent one standard deviation of >10 measurements.
report and those by others in which acoustic techniques are observed to indicate lower elastic moduli than NI. The higher values determined by NI are generally attributed to convolution of the load versus indentation depth response with the composite stiffness of the film and substrate. However, for a few cases, BLS actually indicates Young’s moduli equal to or slightly higher than those determined by NI. This might be a result of assuming $\nu = 0.25$ in the indentation measurements. To account for this, the NI Young’s moduli were recalculated using the values of $\nu$ from BLS. Excluding $\text{SiO}_x\text{C}_{0.8}:\text{H#1}$, which had the highest $\nu$, using the $\nu$ measured by BLS changed the reported NI Young’s moduli by $\leq 0.2$ GPa, which is a small percentage of the difference between the two techniques. For $\text{Si}_{0.2}\text{C}_{0.8}:\text{H#1}$, the NI Young’s modulus was observed to decrease more significantly from 5.4 ± 0.2 to 4.9 ± 0.2 GPa using the BLS $\nu$, but the trend of NI $E >$ BLS $E$ was still maintained. For $\text{SiO}_x\text{C}_{0.8}:\text{H#3}$, we attribute the higher BLS Young’s modulus relative to that from NI to the significant indentation pileup observed during the NI measurements, which might have affected the measured load-indentation depth response.

In comparing BLS and PLU, we observe that the Young’s moduli are comparable but the PLU technique yields slightly lower numbers. This is in contrast to the previous report for non-porous CDO (Ref. 22) and is somewhat surprising given that PLU measures the velocity of longitudinal sound waves, which are directly analogous to the longitudinal organ pipe modes detected in BLS. As with NI, the differences between BLS and PLU are too large to be attributed solely to the assumption of $\nu = 0.25$ in PLU. Interesting, though, the films for which there is the biggest difference in $E$ measured by the two techniques are SiOC:H#3&4 and $\text{SiO}_x\text{C}_{0.8}:\text{H#3}$ and are the highest porosity films. The agreement between BLS and PLU for $\text{SiO}_x\text{C}_{0.8}:\text{H#1}&2$, which have very low porosity, is better. Although this difference in $E$ could be simply a porosity effect, it could also be a laser heating affect. For $\text{SiO}_x\text{C}_{0.8}:\text{H#1}-3$, significant burning of these films under the PLU probe laser was observed. In fact, we were not able to achieve any PLU measurements for SiOC:H#1&2 for this reason. Although no visible laser heating was observed under PLU conditions for SiOC:H#3&4, it cannot be completely ruled out. At the much lower power levels utilized for the BLS study, no damage to the films was evident.

Together with the precision for determining the elastic constants of the porous nano-films, the BLS approach offers several advantages over nanoindentation, which is the most prevalent method for obtaining the stiffness of thin films. As noted, the reliability of nanoindentation data from supported films less than a micron thick is of concern, especially for low modulus low-k porous dielectrics. The stiffness derived from indentation is a combination of the two elastic parameters $E$ and $\nu$. In general, the value of Poisson’s ratio is assumed, and Young’s modulus is computed from the measured indentation profile. A detailed analysis shows that the interaction of the indenter tip with the substrate can in fact make the measured stiffness of the thin film appear to be significantly greater, especially for films less than a micron in thickness. For low-k dielectric materials, which can have values of $E$ from 2 GPa to 15 GPa, this effect can skew the measured $E$ upward as much as 20%. This limitation of nanoindentation is a significant concern, as with each new generation of interlayer dielectrics the films are required to be much thinner than 200 nm and their properties will begin to differ from those of thicker films.

Alternatively, there are two laser-based non-contact techniques available for non-destructively measuring the elastic moduli of thin films: BLS (Refs. 22, 56, 60–62) and PLU. Both are ideally suited for investigations of ultrathin films, as there are no special sample preparation requirements. As mentioned previously, PLU detects longitudinal acoustic waves created through picosecond laser pulses. Several assumptions related to elastic isotropy, Poisson’s ratio, and the film density are required for interpreting the laser ultrasonics data and extracting Young’s modulus. For BLS, the density is also a requirement; however, the simultaneous detection of longitudinal and transverse acoustic waves allows for the determination of both Young’s modulus ($E$) and Poisson’s ratio ($\nu$) as illustrated here and in a previous study. In addition, Brillouin light scattering in particular has been shown to be capable of measuring $E$ for films down to and below 100 nm in thickness in supported and free-standing structures.

For the two laser acoustic methods described above, the detected acoustic signals can be isolated to the film of interest, which implies that the substrate has a minimal effect on the values of the moduli deduced. This strong evanescent character of the guided modes within the Si substrate is consistent with the large acoustic mismatch between the low Young’s moduli of the porous film and values of the Si substrate. These two acoustic methods have each been used to measure the elastic modulus of a low-k dielectric film with precision on the order of $\pm 5%$. It has been shown that Brillouin scattering is capable of determining the dispersion relations of the modified Rayleigh wave of other thin films and their elastic properties down to a few nanometers in thickness.

Figures 5 and 6 summarize, for both the low ($\leq 2\%$) and the high (25%) porosity films, the phase velocities $V (= \omega / (2 \sin \theta))$ of the modes and their variation with $K_{\text{ph}}/h$, the

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**FIG. 5.** The calculated and measured dispersion curves for the principal and higher order modes supported in the $\text{SiO}_x\text{C}_{0.8}:\text{H#2}$ film at the threshold of porosity (2%) as a function of the normalized thickness $K_{\text{ph}}/h$. The solid line identifies $V_{S_{\text{Si}}}^p$, the velocity above which the waves have an oscillatory component in the substrate.
Green’s tensor to fit the measured mode dispersions, confirm modifications in Young’s modulus (8.7–3.5 GPa) and Poisson’s ratio (0.38–0.18) that accompany the introduction of porosity and ensuing reductions in the dielectric constant k. These findings also illustrate the advantage of the non-invasive approach of BLS measurements over nano-indentation methods for determining the mechanical properties of low modulus nano-films being developed as the semiconductor industry moves to the next generation of interlayer dielectrics for emerging large scale integrated technology.

ACKNOWLEDGMENTS

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4 See the 2009 International Technology Roadmap for Semiconductors (ITRS), http://www.itrs.net/.


FIG. 6. The calculated and measured dispersion curves for the principal and higher order modes supported in the SiOC:H#4 film with 25% porosity as a function of the normalized thickness K/h. The solid line identifies V^T in, the velocity above which the waves have an oscillatory component in the substrate.

V. CONCLUSION

We have observed several longitudinal and transverse standing acoustic resonances in ultrathin (<200 nm) porous low-K dielectric films supported on Si. In addition, the transformation of these low lying LSM and TSM modes to acoustic excitations with finite K/h are well accounted for by the projected local density of phonon states and provide for the principal elastic constants of the isotropic porous films. These calculations, based on the associated elastodynamic normalized thickness. In the limit K/h → 0, the lowest mode velocity approaches 4.6 km/s, the non-dispersive Rayleigh wave velocity on an isotropic unlayered Si halfspace, whereas in the opposite limit when K/h tends to large values, this branch tends toward the Rayleigh mode appropriate to a free surface of the bulk low-k material. In the present case, it is evident that the porous film loads the substrate and the free surface of the bulk low-k material. In the present case, it is evident that the porous film loads the substrate and the free surface of the bulk low-k material. In the present case, it is evident that the porous film loads the substrate and the free surface of the bulk low-k material.


