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Dielectric constants and phonon modes of amorphous hafnium aluminate deposited by metal organic chemical vapor deposition

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Dielectric constants and long-wavelength optical phonon modes of amorphous hafnium aluminate films with a maximum aluminum content of 19 at. % are studied by infrared spectroscopic ellipsometry (IRSE). The hafnium aluminate films were prepared by metal organic chemical vapor deposition on silicon substrates. IRSE revealed one polar lattice mode and one impurity-type mode, which show all a systematic shift in frequency with varying Al content. The static dielectric constant decreases from 10.1 for 4.6 at. % Al to 8.1 for 19 at. % Al. The absolute values were found to be between 50% and 70% smaller than the values obtained from electrical measurements. © 2007 American Institute of Physics. [DOI: 10.1063/1.2787962]

The continuous scaling of metal oxide semiconductor field effect transistors is accompanied by a reduction of the gate oxide thickness. SiO₂ has been the gate dielectric material of choice for decades, but a thickness below 1–1.5 nm will generate an excessive leakage current, which will compromise the performance and functionality of the devices. A promising candidate for replacing SiO₂ is HfO₂. HfO₂ is a dielectric material with a static dielectric constant (17–25), with a relatively high free energy of reaction with Si (47.6 kcal/mole at T=727 °C) as compared to TiO₂ and Ta₂O₅, and its relatively large band gap (5.3–5.9 eV).1–3

For minimization of electrical and mass transport along grain boundaries and stabilization of the Si–metal oxide interface, it is preferable that the gate oxide remains amorphous throughout complementary metal oxide semiconductor processing. Unfortunately, amorphous HfO₂ films deposited at low temperatures crystallize during postdeposition annealing. HfO₂ films deposited by metal organic chemical vapor deposition (MOCVD) at higher temperatures or atomic layer deposition typically exhibit a polycrystalline structure. A possible solution is to alloy HfO₂ with Al₂O₃ to form hafnium aluminate, which retains a high relative dielectric constant of ε₉~15 and remains amorphous up to high processing temperatures, for example, up to T=900 °C for an Al content of 31 at. %. ⁴

Furthermore, the incorporation of Al will reduce—in the first instance (6.8 at. % Al)—the leakage current measured on as deposited samples. However, a high Al concentration (e.g., above 31.7 at. %) can result in an increase of the leakage current by two orders of magnitude. HfO₂–Al₂O₃ nanolaminates or multilayer structures have also received recently much attention as they potentially combine the advantages of HfO₂ (thermodynamic stability on Si and high dielectric constant) with those of Al₂O₃ (large band gap of E₉~8.8 eV, large band offset, good barrier properties). These layers are also of specific interest for the realization of metal-insulator-metal capacitors, a key passive device in Si radio-frequency or mixed signal integrated circuit applications.⁵,⁶

This work presents studies of the infrared (IR) active optical phonon modes and dielectric constants of amorphous hafnium aluminate films with a maximum Al content of 19 at. % by infrared spectroscopic ellipsometry (IRSE). Optical studies of HfO₂ in the infrared spectral range were reported previously. For example, transmission intensity measurements were done for HfO₂–SiO₂ films grown by chemical solution deposition (CSD) on Si (Ref. 7) or HfO₂ films grown by chemical vapor deposition on Si/SiO₂Nₓ.⁸ Sintered pellets of ZrO₂–HfO₂ solid solutions were studied by reflection intensity measurements.⁹ Furthermore, phonon mode properties were studied in HfO₂ powder and in Eu-doped HfO₂ sol-gel films by Raman scattering.¹⁰ First-principles studies of structural, vibrational, and lattice dielectric properties of HfO₂ were reported.¹¹ No free-charge-carrier contributions were experimentally identified, but contributions from IR resonance vibrations could be extracted for monoclinic or amorphous HfO₂. Infrared spectra of hafnium aluminate films have not been reported yet. The lack of previous reports and a potential source of information for future investigation of device structures has motivated the present ellipsometry study of the infrared optical response of hafnium aluminate films on silicon. Note that IRSE can be, in principle, applied to determine the properties of very thin films despite the fact that light wavelengths exceed the layer thickness by several orders of magnitude.¹²

Hafnium aluminate films were deposited on Si substrates by liquid injection MOCVD with an Aixtron AIX 200FE Atomic Vapor Deposition (AVID™) reactor fitted with a “Trijet”™ injector system. The Hf and Al precursors are [Hf(OCMe₂CH₂OMe)₃] and [Al(OPr)₃], respectively. The precursors are dissolved in heptane at a concentration of 0.1M. A constant injection rate of [Hf(mmp)]₂ was used, while the [Al(OPr)₃] mole fraction was varied. The substrate and evaporator temperatures were T=500 °C and...
T=200 °C, respectively. The reactor pressure was $p=5$ mbars, and the argon and oxygen flow was chosen to be 200 and 100 SCCM (SCCM denotes cubic centimeter per minute at STP) respectively. The concentrations of the precursors were carefully monitored during the deposition. The homogeneity and Al content of the films were determined by spectroscopic ellipsometry in the ultraviolet and visible spectral regions and by Auger spectroscopy, respectively.13

Spectroscopic ellipsometry is a well-known technique for the determination of the dielectric function (DF) and thickness $d$ of thin films within layered samples.12 The ellipsometric parameters $\Psi$ and $\Delta$ are related to the complex reflectance parameter $r=p/r_s=\tan \Psi \exp(i\Delta)$, where $r_p$ and $r_s$ are the reflection coefficients for light polarized parallel ($p$) and perpendicular ($s$) to the plane of incidence, respectively. IRSE spectra are analyzed by a model analysis using a model dielectric function (MDF). The IR DF is sensitive to phonon and free-carrier contributions. The hafnium aluminate films were highly electrically resistive, and no free-charge-carrier contributions were detected. Hence, the following MDF is used.12

$$\varepsilon(\omega) = \varepsilon_\infty \left[ \frac{\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i \gamma_{LO} \omega} \left( 1 + \frac{i \delta \gamma - \delta \omega^2}{\omega^2 + i \gamma_{TO,IM} \omega - \omega_{IM}^2} \right) \right].$$

(1)

Equation (1) considers electronic contributions by including the high-frequency MDF limit $\varepsilon_\infty$ and contributions due to one lattice and one impurity-type mode. An anharmonic oscillator with Lorentzian broadening is used to describe the polar lattice mode, which splits into transverse optical (TO), longitudinal optical (LO), $\gamma_{TO}$, and $\gamma_{LO}$ phonons. The impurity-type mode ($\gamma_{IM}$) describes modes with low polarity, which contribute to the DF as a small perturbation only.14,15 Lattice imperfections or alloying disorder can induce sublattice modes of small polarity. Equation (1) holds for the frequencies $\delta \omega^2 = \omega_{LO,IM}^2 - \omega_{TO,DM}^2$ and the broadening parameters $\delta \gamma = \gamma_{LO,IM} - \gamma_{TO,IM}$. IRSE spectra were recorded with an IR wvASE (J. A. Woollam Inc.) at room temperature, with a spectral resolution of 8 cm$^{-1}$, in the spectral range from 360 to 3000 cm$^{-1}$, and at two angles of incidence $\Phi_0=70^\circ$ and 75°.

The static dielectric constant $\varepsilon_0$ can be calculated from $\varepsilon_\infty$, $\omega_{TO}$, and $\omega_{LO}$ by the Lydanne-Sachs-Teller relation

$$\varepsilon_0 = \varepsilon_\infty \prod_{i=1}^l \frac{\omega_{LO,i}^2}{\omega_{TO,i}^2}.$$  

(2)

The static dielectric constant $\varepsilon_0$ can be referred to the relative dielectric constant $\varepsilon_r$, for which the notations $k$ or $\kappa$ are also often used in the literature.

Figure 1 shows the IRSE spectra of the hafnium aluminate films on silicon. A good agreement between experimental and model data can be seen. The IRSE analysis revealed one polar lattice mode and one impurity-type mode. The frequencies of the lattice mode and of the aluminium-induced impurity mode reveal a consistent blueshift with increasing Al content. This blueshift reflects the substantial decrease of the host lattice mass by substitution of Hf with Al content. The increment of the broadening parameters with increasing Al content is assigned to the increasing disorder due to alloying.

In Fig. 3, the high-frequency dielectric constants $\varepsilon_\infty$, as determined by IRSE, and the static dielectric constants $\varepsilon_0$ calculated by the Lydanne-Sachs-Teller relation [Eq. (2)], are summarized. For both $\varepsilon_\infty$ and $\varepsilon_0$, a systematic decrease with increasing Al content can be seen. The same trend was found

![FIG. 1. Experimental (dotted lines) and best-match calculated (solid lines) IRSE $\Psi$ and $\Delta$ spectra of hafnium aluminate films on silicon. The angle of incidence is $\Phi_0=70^\circ$. TO, LO, and IM modes are indicated by vertical dashed lines.](Image)

TABLE I. Best-match MDF parameters and film thickness $d$ for the hafnium aluminate films. Error bars in parentheses represent the 90% confidence limits.

<table>
<thead>
<tr>
<th>Film Thickness</th>
<th>$\varepsilon_\infty$</th>
<th>$\omega_{TO}$ (cm$^{-1}$)</th>
<th>$\gamma_{TO}$ (cm$^{-1}$)</th>
<th>$\omega_{LO}$ (cm$^{-1}$)</th>
<th>$\gamma_{LO}$ (cm$^{-1}$)</th>
<th>$\omega_{IM}$ (cm$^{-1}$)</th>
<th>$\gamma_{IM}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6 at. % Al</td>
<td>3.339 (0.008)</td>
<td>419 (4)</td>
<td>317 (6)</td>
<td>733 (3)</td>
<td>383 (5)</td>
<td>881.2 (0.9)</td>
<td>227 (7)</td>
</tr>
<tr>
<td>12.8 at. % Al</td>
<td>3.089 (0.008)</td>
<td>448 (5)</td>
<td>476 (11)</td>
<td>803 (3)</td>
<td>624 (14)</td>
<td>907.0 (0.5)</td>
<td>304 (6)</td>
</tr>
<tr>
<td>19 at. % Al</td>
<td>2.916 (0.008)</td>
<td>553 (4)</td>
<td>614 (18)</td>
<td>921 (7)</td>
<td>796 (21)</td>
<td>925.0 (0.3)</td>
<td>373 (7)</td>
</tr>
</tbody>
</table>

$\varepsilon_\infty$ and $\omega_{TO}$ by the Lydanne-Sachs-Teller relation [Eq. (2)].

$\varepsilon_0$ Calculated from $\omega_{TO}$ and $\omega_{LO}$ by the Lydanne-Sachs-Teller relation
in C-V measurements on the same samples.\textsuperscript{13,16} However, the dielectric constants were found to be higher (between 50% and 70%) than reported here. The strong discrepancy between the static dielectric constants from previous electrical and present infrared measurements is not clear at this point. Experimental conditions under which the quantities are determined affect the accuracy of the results. For instance, contact preparation, interface, and built-in charges can result in an apparent increase of the material’s relative dielectric constant from electrical measurements. Furthermore, the evaluation of the previous C-V data analysis cannot be fully correct because erroneous thickness values were assumed due to an interface region which cannot be accessed. Therefore, the C-V data represent only effective dielectric constant values. Note also that the electrical measurements were typically done at low frequencies between 50 and 100 kHz, which correspond to wavenumbers between \(1.7 \times 10^6\) and \(3.3 \times 10^6\) cm\(^{-1}\) or wavelengths between \(6 \times 10^8\) and \(3 \times 10^9\) \(\mu m\).

Infrared optical studies are known to be an accurate and appropriate tool for the determination of the static and high-frequency dielectric constants. Infrared ellipsometry, which determines thickness and optical constants from semiconductor thin films independently, has been proven very recently to yield accurate results of the static and high-frequency dielectric constants for numerous semiconductor materials and thin film structures.\textsuperscript{12} Recently, Momida \textit{et al.} presented first-principles studies of the dielectric constants of amorphous hafnium aluminate.\textsuperscript{17} They reported also values larger than those measured here; even measurements with a far-infrared ellipsometry setup in the spectral range from 150 to 600 cm\(^{-1}\) did not show additional modes.

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