

# Characterization of metal oxide nanofilm morphologies and composition by terahertz transmission spectroscopy

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An all-optical terahertz absorption technique for nondestructive characterization of nanometer-scale metal oxide thin films grown on silicon substrates is described. Example measurements of laser-deposited TiO<sub>2</sub> and atomic layer-deposited films of HfO<sub>2</sub> are presented to demonstrate applicability to pure Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and VO<sub>x</sub> and mixed combinatorial films as a function of deposition conditions and thickness. This technique is also found to be sensitive to HfO<sub>2</sub> phonon modes in films with a nominal thickness of 5 nm.

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Metal oxide thin films find applications in a variety of areas including microelectronics, read-write heads for magnetic recording, electroluminescent screens, and optical filters. An important requirement for controlling the dielectric and material properties of metal oxide thin films is the ability to assess film thickness, composition, and crystallinity. Far-infrared (terahertz, THz) absorption spectroscopy performed in the 1–21 THz spectral region (33–700 cm<sup>-1</sup>) has been shown to be extremely sensitive to the compositional details and local environmental conditions of numerous materials [1]. Spectral features in the higher end of this wavelength range typically arise from internal vibrational modes (for molecular solids), while cooperative intermolecular or interatomic optical or acoustic phonon modes occur at lower frequencies (for typical inorganic materials). Often the absorption cross sections for molecular crystal phonon modes are small because the transition dipole moments for these low-frequency motions are negligible. On the other hand, long-range phonon mode absorptions in semiconductor and related inorganic systems can be quite large, especially if the materials contain partially charged heavy metal ions. THz spectroscopy is also noncontact, nondestructive, and spatially resolved (on millimeter length scales). During an early study at National Institute of Standards and Technology (NIST) of hafnium oxide films grown on transparent silicon wafer substrates, it was found that ~200 μm thick films exhibit abnormally strong, clearly identifiable absorption features in the THz spectral range. These features were subsequently modeled and assigned as transverse phonon modes by using solid-state density functional theory with periodic boundary conditions (via the software package VASP) [2]. While earlier investigations focused on measurement of pure bulk, crystal, or liquid-phase samples, the application of

THz spectroscopy to thin-film libraries and combinatorial mixed-metal oxides of nanometer-scale thickness have not been widely reported. Hence, our purpose in this Letter is to describe the THz spectroscopic measurement approach, including experimental details and limitations, as applied to thin-film characterization.

TiO<sub>2</sub> and HfO<sub>2</sub> films were selected to illustrate this technique for the following reasons. TiO<sub>2</sub> exhibits a number of low-wavenumber (i.e., below ~400 cm<sup>-1</sup>) phonon modes [3–8] to which conventional mid-infrared spectroscopy is generally insensitive. The identification of these phonons in TiO<sub>2</sub> (and related metal oxide materials) is an important capability for resolving materials characterization issues and validating lattice dynamics calculations. For TiO<sub>2</sub>, the rutile phase exhibits a relatively strong absorption at ~180 cm<sup>-1</sup> [3–10], while the anatase phase does not exhibit any modes below 260 cm<sup>-1</sup> [5–7]. Obviously, the identification of the 180 cm<sup>-1</sup> mode would be useful in distinguishing the presence or absence of rutile. Unfortunately, except in a previous report by some of us and our coworkers [10], this mode had not been previously observed by using transmission THz spectroscopy. However, in [10] the mode was not identified, and the peak wavenumber was not reported. Hence, the reported wavenumber value has originated only from curve fits to relatively featureless regions of far-infrared reflection spectra [3,4,8]. Combinatorial films of Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and VO<sub>x</sub> spectra obtained under similar deposition conditions also exhibit sharp and readily identifiable features between 200 and 600 cm<sup>-1</sup> that change slightly in peak frequency and intensity with deposition temperature [9]. HfO<sub>2</sub> films investigated here were deposited by atomic layer deposition (ALD). ALD was utilized because this technique produces nanometer-thick films with a high degree of thickness control [11]. Hence,

the expected sensitivity of THz absorption spectroscopy can be examined by applying this technique to ultrathin ALD films.

The  $\text{TiO}_2$  films investigated in this work were deposited by using pulsed laser deposition, as previously described [10]. All  $\text{TiO}_2$  films were deposited at different locations on the same silicon wafer substrate (double-side polished,  $>50 \Omega \text{ cm}$  resistivity,  $500 \mu\text{m}$  thickness). Substrate temperatures ranged from 573 to 1023 K with deposition, starting at 1023 K and decreasing the temperature by 50 K for each subsequent deposition. All  $\text{TiO}_2$  films were nominally 200 nm thick. The  $\text{HfO}_2$  ALD deposition process was previously described [12].  $\text{HfO}_2$  films were deposited on (100) silicon wafers (double-side polished, either  $>1000 \Omega \text{ cm}$  or  $>10 \Omega \text{ cm}$  resistivity). Prior to ALD, wafers were dipped in a 2% HF solution for 30 s and then exposed to ozone for 4 min. For this investigation, films were grown at substrate temperatures of either 503 K or 573 K, and nominal film thicknesses varied from 5 to 40 nm.

Terahertz absorption measurements were made with a Fourier transform infrared spectrometer modified with a silicon-coated Mylar broadband beam splitter and a room-temperature, deuterated triglycine sulfate thermoelectric detector with a high-density polyethylene window. The instrument was purged with dry nitrogen for 10 min to eliminate low-frequency (1–3 THz) water vapor interference. All spectra were taken with the sample at room temperature and represent an average of 64 interferometric scans ( $\sim 3$  min per scan data collection time) with a spectral resolution of  $8 \text{ cm}^{-1}$  (to eliminate substrate interference fringes). Samples were placed normal to the beam measured to be approximately 2 mm FWHM in diameter and position locatable to within 1 mm on the wafer surface. For pulsed laser deposition  $\text{TiO}_2$ , a reference spectrum was obtained by placing an unexposed region of the silicon substrate wafer into the beam path. For ALD  $\text{HfO}_2$ , reference spectra were obtained by using identical substrates cleaned and ozone exposed under conditions nominally identical to those for the substrates on which ALD was performed. Transmission values were converted to optical density (OD) units using the ratios of sample transmission  $T$  (film on substrate) to the reference transmission  $T_o$  (substrate only), according to  $\text{OD} = -\log_{10}(T/T_o)$ . The optical density uncertainty (approximately  $\pm 0.01$ ) increases for frequencies  $<150 \text{ cm}^{-1}$  and  $>575 \text{ cm}^{-1}$  because of this referencing procedure and low instrument light levels in these extremes.

Figure 1 shows the spectra of six  $\text{TiO}_2$  films as a function of substrate temperature during deposition [10]. The spectra of films deposited at temperatures above 673 K exhibit three relatively intense features centered at 180, 380, and  $500 \text{ cm}^{-1}$  that are attributed to the rutile  $E_u$  transverse optical phonon modes [3,4,8]. In these spectra, relatively weak features and shoulders are also observed near 390, 475, and  $575 \text{ cm}^{-1}$ . The 390 and  $475 \text{ cm}^{-1}$  shoulders are attributed to the rutile  $E_u$  longitudinal optical phonon

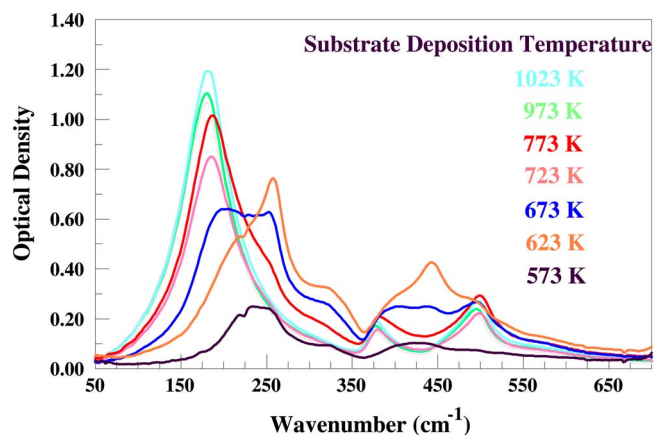


Fig. 1. (Color online) Terahertz absorption library spectra of  $\text{TiO}_2$  pulsed laser deposition films on silicon as a function of substrate temperature. Varying the temperature yields spectra for the rutile (e.g., 180, 375, and  $475 \text{ cm}^{-1}$  bands) and anatase (e.g., 250, 330, and  $475 \text{ cm}^{-1}$  bands) form of  $\text{TiO}_2$  that are mixed at the 623 K deposition temperature [10]. All films were nominally 200 nm thick.

modes [3,4]. The weak peak at  $575 \text{ cm}^{-1}$  is not assigned but may arise from so-called secondary modes [4]. The absence of  $A_{2u}$  modes (the only other infrared-active symmetry for  $\text{TiO}_2$ ) is a result of the measurement geometry employed in this work. The spectrum of the film deposited at 623 K exhibits two relatively intense features near 255 and  $450 \text{ cm}^{-1}$  attributed to the anatase  $E_u$  transverse optical phonon modes [5–7]. Relatively weak shoulders are also observed near 325, 400, and  $500 \text{ cm}^{-1}$ . The shoulder at  $325 \text{ cm}^{-1}$  is attributed to the anatase  $E_u$  longitudinal optical phonon mode [5–7]. The origins of the 400 and  $500 \text{ cm}^{-1}$  features are unknown. These modes are observed at wavenumbers similar to the rutile  $E_u$  longitudinal optical phonon modes; however, the corresponding rutile  $E_u$  transverse optical phonon modes (e.g., at  $180 \text{ cm}^{-1}$ ) are not observed. These modes may be due to a crystal structure intermediate to anatase and rutile that is involved in the anatase-to-rutile phase transformation. The spectrum of the film deposited at 673 K exhibits features attributed to rutile and anatase near 240, 325, and  $425 \text{ cm}^{-1}$ . The wavenumber positions suggest an anatase-like phase (see the 673 K deposition spectrum); however, the broad features indicate a disordered and/or amorphous structure. These observations are consistent with x-ray diffraction measurements of these same films, as previously reported [10].

Figure 2 shows the spectra of three  $\text{HfO}_2$  films with a nominal thickness of either 20 or 40 nm and deposited at a substrate temperature of 503 or 581 K. The spectra of the 20 nm thick film deposited at 505 K, and the 40 nm thick film deposited at 503 K exhibit a broad, featureless absorption centered at  $\sim 324 \text{ cm}^{-1}$ . The appearance of these spectra indicates that films deposited under these conditions are all amorphous [13]. The spectrum of the 40 nm thick film deposited at 581 K exhibits reasonably resolved peaks around 255, 324, 395, and  $506 \text{ cm}^{-1}$  with other unresolved features being evident. The appearance of this spec-

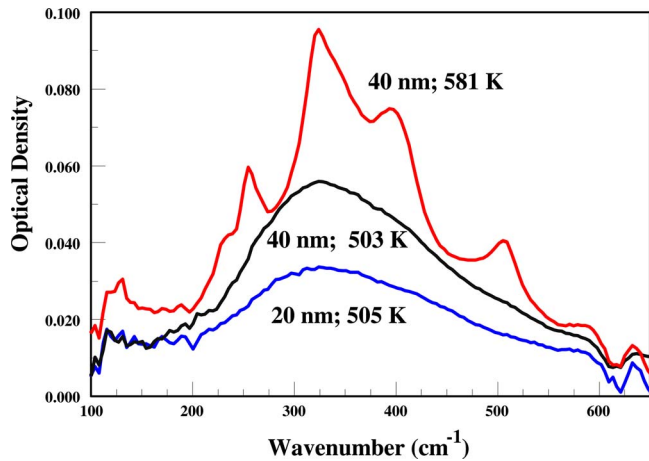


Fig. 2. (Color online) Terahertz absorption spectra of  $\text{HfO}_2$  films grown by atomic layer deposition on silicon substrates exhibiting spectral structure for ordered crystalline films compared with amorphous depositions at lower temperatures. Results for a 20 nm thick film grown at 581 K overlap the 20 nm 505 K data.

trum is attributed to the presence of crystalline  $\text{HfO}_2$ , and these peak wavenumbers are in good agreement with those reported for monoclinic  $\text{HfO}_2$  in this wavenumber range [13–15]. The distinct absorption features are also superimposed on a broad featureless background (similar to the other spectra), suggesting that the thick, high-temperature film is composed of both crystalline and amorphous hafnium oxide, possibly arising from oxide crystallites embedded in an amorphous matrix. The appearance of crystalline features in the spectrum of the 40 nm thick film deposited at 581 K but not in the spectrum of the 20 nm thick film deposited at the same temperature (overlapping the 20 nm 505 K film response, not shown) permits estimating the boundaries for the critical thickness for crystallization of  $\text{HfO}_2$  deposited under these conditions.

Last, Fig. 3 shows the spectra of amorphous  $\text{HfO}_2$  films with nominal thicknesses ranging from ~5 to

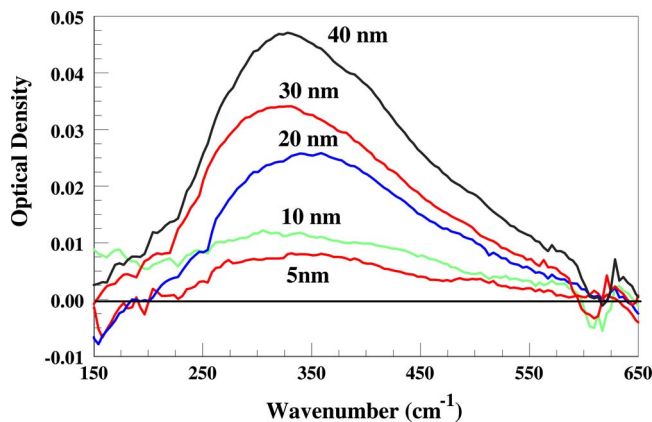


Fig. 3. (Color online) Terahertz absorption spectra of  $\text{HfO}_2$  ALD films on silicon ( $T=503$  K) as a function of deposition time (thickness). Identification of amorphous films (broad spectral absorption) with thicknesses down to 5 nm are resolved via optical density above the zero baseline.

40 nm (all films deposited at 503 K). As can be seen, the optical density is clearly proportional to the layer thickness, and it is possible to observe the broad, featureless (amorphous) peak for films at least as thin as 5 nm by using this technique.

Direct optical THz transmission spectroscopy of silicon-supported metal oxide films has been demonstrated by characterizing pulsed laser deposition  $\text{TiO}_2$  and ALD  $\text{HfO}_2$  nanolayer films.  $\text{TiO}_2$  phonon modes were observed at wavenumbers too low to be observed with conventional mid-infrared spectroscopy. This capability was shown to be useful in distinguishing between the anatase and rutile  $\text{TiO}_2$  phases. This technique was also demonstrated to be sensitive to  $\text{HfO}_2$  phonon modes in films with a nominal thickness of 5 nm. This sensitivity is important, since nanoelectronics transistor gate dielectric applications involve metal oxide films in the 1–10 nm range. Hence, this approach offers great promise for metal oxide thin-film characterization during online growth. Investigations of nanofilms as a function of incident angle (to determine phonon mode symmetries) and mixed metal oxide combinatorial films by using this method are under way.

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