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Spectroscopic Creativity

Analysis of Monomolecular Layers on Silicon Using an Optimized Grazing Angle ATR Accessory and FTIR Spectroscopy

Kenneth D. Kempfert, PIKE Technologies

Spectroscopic probing of very thin films including monomolecular layers on silicon (Si) has become a very important analytical technology with emerging applications in the semiconductor, biosensor, and telecommunications industries. Traditional methods of analysis of very thin films on reflective surfaces have generally involved characterization of the surface via grazing angle specular reflectance Fourier transform infrared (FTIR) spectroscopy (1). In the case of measurements on reflective surfaces such as gold or aluminum with high reflectivity, grazing angle specular reflectance analysis is a good measurement choice because of the significant sensitivity increase. When the very thin layer is either bonded or coated onto a Si substrate, specular reflectance is more difficult due to lower reflectivity and because Si has several absorbance bands in the mid-infrared spectral region.

Several researchers have reported success using attenuated total reflectance (ATR) at high incident angle (grazing angle) for the measurement of monolayers and thin films on Si. The first reported measurements were done using multiple reflection ATR using a germanium (Ge) crystal at 60° angle of incidence (2). Subsequent publications report upon using single reflection ATR with Ge crystal at either 60 or 65° and parallel (p) polarization (3,4). Lummerstorfer and Hoffmann compared results for measurements of monolayers on Si using grazing angle specular reflectance, and ATR at 65°. Their publication finds a sensitivity enhancement of up to 15× for ATR vs. grazing angle specular reflectance (5).

This application note describes the use of a variable angle specular reflectance accessory coupled with a single reflection ATR crystal for the analysis of thin films and monolayers on Si.

Figure 1: VeeMAX II with Single Reflection ATR Crystals.

Experimental

All measurements were done using a PIKE Technologies VeeMAX II™ equipped with a 60° single reflection Ge ATR crystal, a high pressure clamp with 7.8 mm pressure tip, and an integrated zinc Selenide (ZnSe) wire grid polarizer set for p polarization — shown in Figure 1. This variable angle accessory with set angles of incidence ranging from 30 to 80° can be used for specular reflectance measurements as well as ATR measurements (6).

Samples were placed face down onto the ATR crystal and no purge loss occurred when samples were changed. The VeeMAX ATR crystal employed in these measurements was 20 mm diameter and the accessory had an easily accessible sample area for analysis of small or large samples.

Success of the grazing angle ATR measurement depends upon intimate contact of the sample with the ATR crystal. Where the sample is a few nanometers thick and the sample substrate is as hard as Si, a single dust particle could prevent a successful measurement. To ensure a successful measurement, we place a 1″ × 3″ piece of lens tissue (Type 1, Class 1, Universal Photonics, 495 W. John St., Hicksville, NY 11801, www.universalphotonics.com) over the ATR crystal and then place the sample face down over the lens tissue. Light pressure is applied to the back of the Si sample and the lens tissue is pulled out, which cleans the interfacial surfaces and ensures intimate contact between the thin film and the ATR crystal. Once the lens tissue is removed, the VeeMAX II pressure clamp is increased to its maximum force and the spectrum is collected.

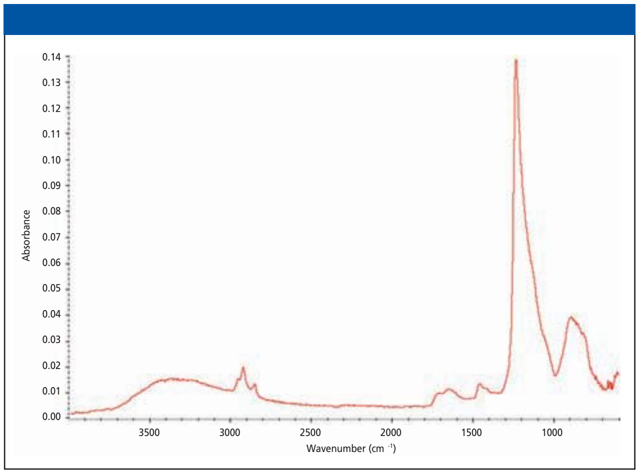

Figure 2: Functional organic monolayer on Si measured on VeeMAX II ATR.

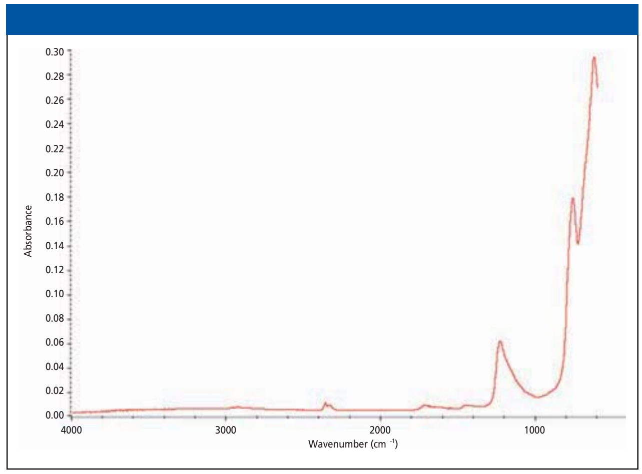

Figure 3: Grazing angle ATR spectrum of 50-nm thick layer of HfO_2 on Si.

FTIR measurements were done at 4 cm^{-1} spectral resolution using a DLaTGS detector. Data acquisition time was 4 minutes for background and sample.

Results

Two different samples are shown here to demonstrate this application. The first was a functional organic monolayer on silicon substrate, approximately 2 cm × 2 cm and 0.4 mm-thick — spectrum shown in Figure 2.

The Si-O stretching band at 1238 cm^{-1} is the strongest absorbance band in the spectrum. The C-H stretching bands at 2956, 2926, and 2855 cm^{-1} are readily apparent, as are additional absorbance bands in the fingerprint region of the spectrum.

The second sample is a thin layer (50 nanometers) of hafnium oxide (HfO_2) on silicon. In this spectrum in Figure 2 we see strong absorbance bands for the HfO_2 at 759 and 619 cm^{-1}. In this spectrum the Si-O stretching band is located at 1231 cm^{-1} and is seen as relatively weaker compared to the HfO_2 bands.

Summary

Excellent quality FTIR spectra can be measured from monomolecular layers and thin films on Si substrates by using the VeeMAX II with a 60° Ge ATR crystal and p polarization.

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PIKE Technologies
2901 Commerce Park Drive, Madison, WI 53719
Tel. (608) 274-2721, Fax (608) 274-0103
sales@piketech.com, www.piketech.com