

Polarization modulated infrared spectroscopy of thin films at the nanometer scale

This application note illustrates how the KSV NIMA PM-IRRAS can be used to characterize ultra thin films in order to obtain information such as molecular orientation and chemical composition.

Introduction

Precise methods for thin film surface preparation and characterization are key factors in modern nanotechnology. Polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS) is a powerful method for measuring FT-IR from molecules on substrates. From the surface specific IR-spectrum obtained with this method it is possible to deduce chemical composition of films, orientation of molecules and relative amount of material on the surface. This is important in many industrial areas utilizing or planning to utilize nanofabrication and self assembly, molecular electronics, coatings, corrosives, sensors and catalysis.

The Langmuir-Blodgett (LB) deposition technique is a way to create one molecule thick films. It offers control over the molecular orientation and film thickness in the molecular scale. Stearic acid (SA) was used as a model compound to present how the KSV NIMA PM-IRRAS can be used to characterize nanofabricated thin films. A self-assembled film of a well known anticorrosive compound for copper containing metals, methylbenzo triazole (MBT), was created on brass and the layer was studied with the KSV NIMA PM-IRRAS.

The KSV NIMA PM-IRRAS is a FT-IR spectrometer mounted on a goniometer and equipped with a photoelastic modulator. The IR-light is modulated at high frequency (different from the FT-IR source frequency) and at the signal processing the two are separated electronically. The result is that two IR-spectra are obtained simultaneously, a so-called sum spectrum and difference spectrum. Because p- and s-polarized light reflect differently from surfaces, any differences between the two spectra come from surface specific absorptions. Furthermore on conductive surfaces so called mirror effect will enhance p-polarized components and diminish s-polarized of dipoles, which makes it possible to deduce conformational information of molecules from the spectrums [1].

Also the use of sum and difference spectra diminishes environmental effects on the spectra, such as CO₂ and water vapor, and removes the need for protective gasses in reflection measurements. This property allows the KSV NIMA PM-IRRAS to have a very open architecture, enabling measurements from liquid surfaces and solid samples of almost any size. The open design also allows combined use of external UV light source, heater or other complementary equipment.

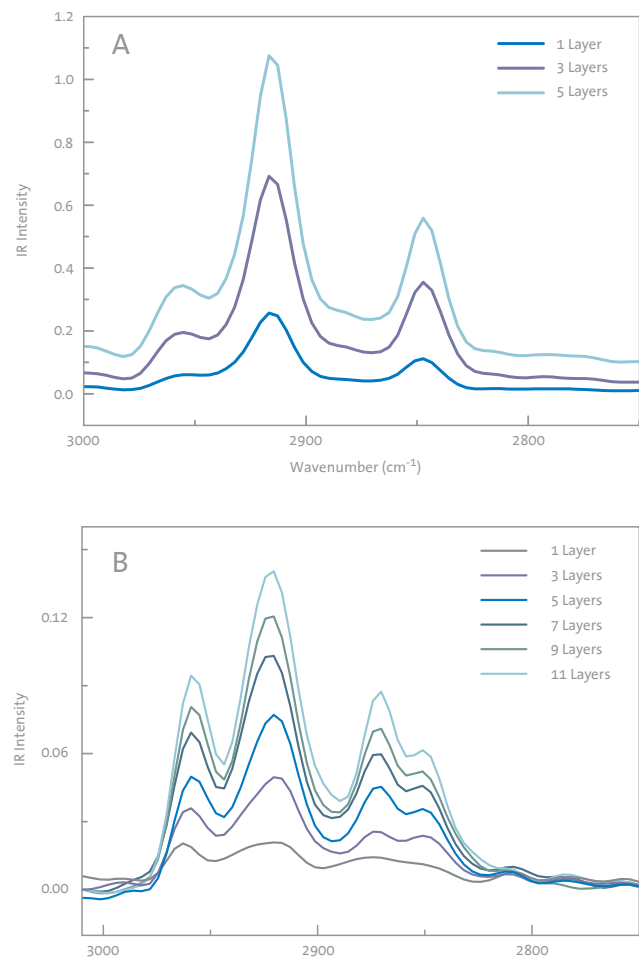
Materials and methods

SA films were created by LB-method from 0.1 mM CdCl₂ subphase onto a glass substrate that had a 300 nm gold coating. Two different sets of LB films were prepared, one with subphase pH 2 and other with pH 6. PM-IRRAS measurements were performed on the films after each LB-cycle.

MBT was self assembled by dipping a brass substrate into a 60 mg/L solution dissolved in ethanol for one hour.

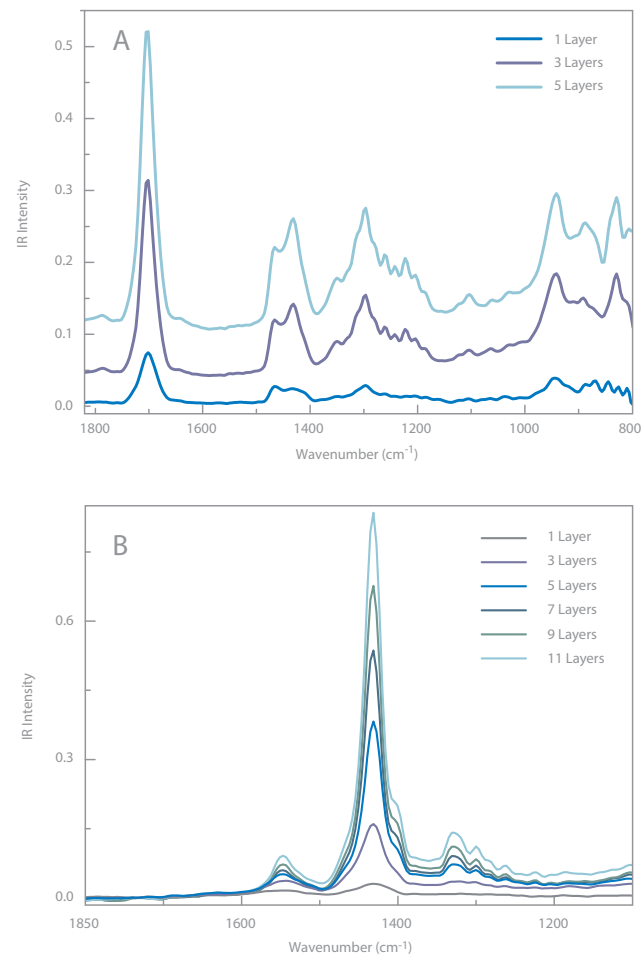
Results and discussions

From the FT-IR spectra of deposited SA LB-film, it is possible to distinguish CH_3 symmetric stretch (2960 cm^{-1}), CH_2 symmetric (2850 cm^{-1}) and asymmetric (2918 cm^{-1}) stretches (Figure 1).



[Figure 1]: PM-IRRAS spectra of SA Langmuir-Blodgett films of increasing thickness on gold at (A) pH 2 and (B) pH 6 in the C-H stretch region

For the LB films made from pH 2, the $\text{C}=\text{O}$ stretch (1710 cm^{-1}), COO^- symmetric stretch (1430 cm^{-1}) and CH_2 wagging and twisting ($1200\text{--}1350\text{ cm}^{-1}$) were identified (Figure 2A). For pH 6 films there was no $\text{C}=\text{O}$ stretch, but the COO^- symmetric stretch was much more pronounced and also COO^- asymmetric stretch (1540 cm^{-1}) was identified (Figure 2B).



[Figure 2]: PM-IRRAS spectra of SA Langmuir-Blodgett films of increasing thickness on gold at (A) pH 2 and (B) pH 6 between 1800 and 800 cm^{-1}

Peak intensity increased with layer number with excellent linearity, as shown in Figure 3.

MBT PM-IRRAS spectrum shows peaks at 2920 cm^{-1} and 2850 cm^{-1} (Figure 4). Even though these are usually assigned to CH_2 stretches, bulk spectra of MBT from KBr disk shows CH_3 peaks at 2914 and 2829 cm^{-1} , and toluene bulk spectra shows 2920 and 2973 cm^{-1} . [2]

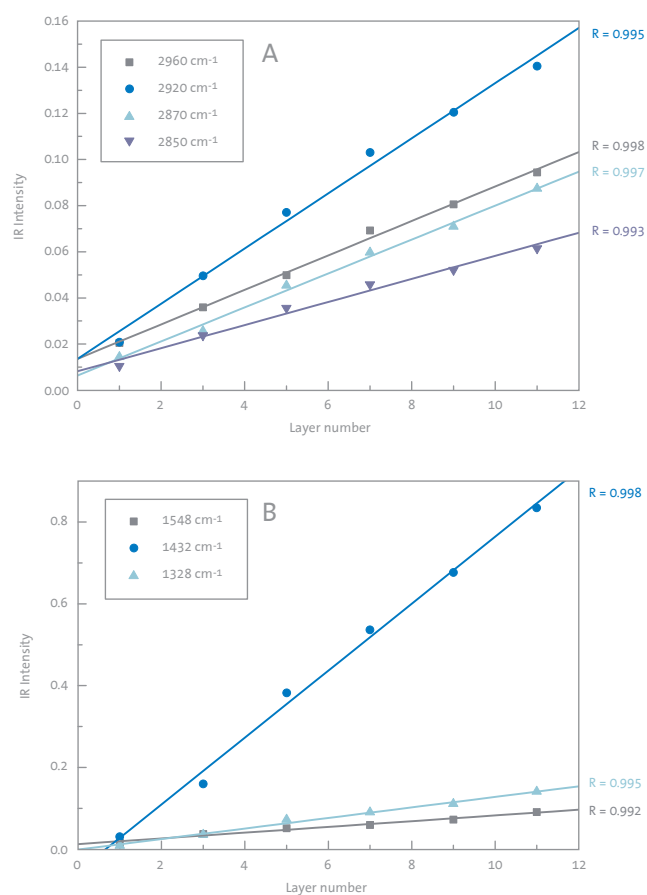
Based on this, the peaks can be assigned to the CH_3 group of MTB. Other peaks in the MTB spectrum were assigned to the aromatic part of the molecule (1517-1600, 1443, 1405 and 1245-1100 cm^{-1}) based on the bulk spectrum of MTB and IR-tables from literature [3]. The fact that C-H stretch from benzene ring is missing from the spectrum (at 3030 cm^{-1}) indicates that the aromatic ring has planar orientation in relation to the metal surface. This is due to the Surface Dipole Selection Rule effect that enhances the p-component and cancels out s-component of electric dipole on conducting surfaces. [1] No PM-IRRAS or IRRAS studies of MTB were found from literature, and to our best knowledge this is the first time such experiments are reported.

Conclusions

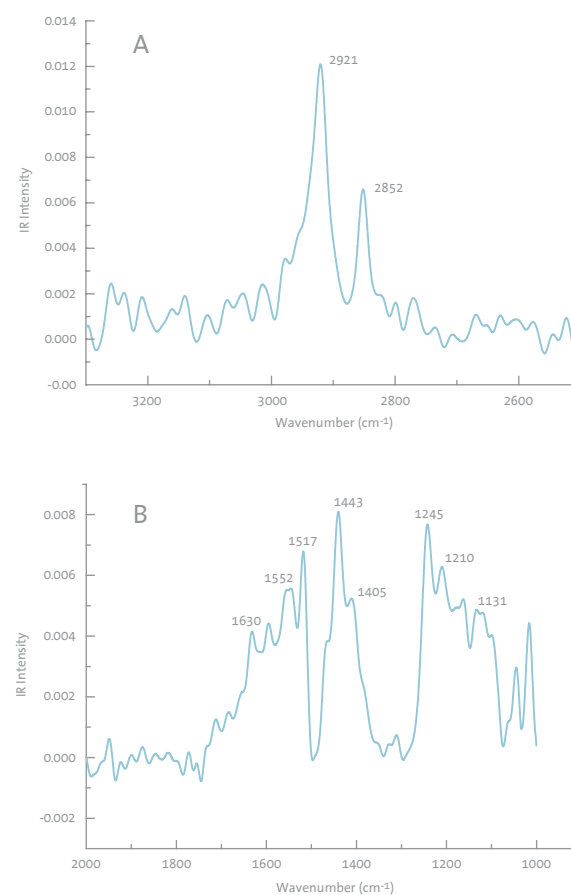
The PM-IRRAS method was found to be excellent for FT-IR experiments of nanometer scale thin films. It was possible to acquire FT-IR spectrums of films of around 2 nm thick, and also deduce molecular orientation from the experiments. Linear correlation between LB layer number and peak intensities was found. This demonstrates that the KSV NIMA PM-IRRAS is a powerful tool for thin film characterization and analysis. The measurements are fast and simple to perform thanks to KSV NIMA PM-IRRAS unique design.

References:

- [1] Griffiths, P and Haseth, J., Chemical Analysis 83: Fourier Transformation Infrared Spectrometry, Wiley, 1983, Chapters 8 and 17
- [2] SDBS, Available at: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng [Accessed on 30 March 2010]
- [3] Hase, T., Tables for Organic Spectrometry, Otatietao, 1992



[Figure 3]: Linear fits of peak intensity versus layer number of SA deposited at pH6. (A) C-H region and (B) between 1800 and 1200 cm^{-1}



[Figure 4]: PM-IRRAS spectra of self assembled MBT film on brass (A) C-H region and (B) between 2000 and 1000 cm^{-1}