

## Measurement of thin film by Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS)

### Introduction

Several industrial products utilizing the advanced functionalities of thin films such as electric, optical and/or mechanical properties are now getting more and more popular in the market and techniques on generation and evaluation of film are steadily improved in accordance with better quality of products. The Infrared spectroscopy is known as one of the evaluation methods of such thin film providing information on molecular structure and orientation along with optical thickness and electric properties. Especially, Infrared Reflection-Absorption Spectroscopy (IRRAS) method enables to implement molecular structure analysis of a very thin film with a thickness of tens of angstroms on metal substrates. However, there is a growing need for higher sensitivity measurement and also process monitoring of film generation because the recent devices require higher performance and higher functionality. In order to meet such requirement, a monitoring system for film generation in vacuum chamber has been developed by using Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) with greater sensitivity than ordinary IRRAS. This report explains the outline of the system as well as the data for measurement of thin film using PM-IRRAS.

### Principle of PM-IRRAS

IRRAS provides IR spectra measurement of thin film on metal substrates with high sensitivity by using p-polarized light parallel to incidence plane. The p-polarized light ingenerates the electric field of stationary vibration which increases sensitivity (See Fig.1). This allows film thickness measurement in Å level. However, absorption peaks obtained by IRRAS are usually very small, which may often require long time accumulation. In addition, both of reference and sample substrates need to be measured. For these reasons, spectrum is significantly affected by absorption of H<sub>2</sub>O and CO<sub>2</sub> in atmosphere.

On the other hand, PM-IRRAS is a method of finding intensity difference of s- and p-polarized lights ( $\Delta I = I_p - I_s$ ) which is vertical and parallel to incidence plane respectively by using Photoelastic Modulator (PEM). As s-polarized light does not ingenerate the electric field of stationary vibration, absorption is much smaller than that of p-polarized light. In addition, in PM-IRRAS, the sum of s- and p-polarization signal ( $\Sigma I = I_p + I_s$ ) is used as reference and so there is no need to measure reference substrates. Hence, the effect due to absorption of H<sub>2</sub>O and CO<sub>2</sub> in atmosphere can be decreased greatly. Since the measurement of reference substrate is not needed, the measurement results can be free from effect of difference between substrates and the measurement time can be shortened.

Additionally, this PM-IRRAS measurement system allows higher sensitivity by detecting small  $\Delta I$  signal using direct lock-in detection by adopting dual modulation spectroscopy of FT/IR interferometer and PEM. Fig. 2 shows measurement results of PMAA thin film on Al mirror obtained by IRRAS and PM-IRRAS while other conditions are the same. Spectra obtained using PM-IRRAS is several times better in S/N than IRRAS.

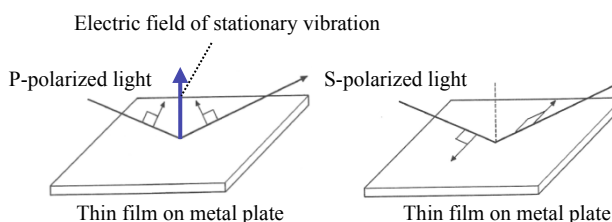


Fig. 1. Diagram of IRRAS method

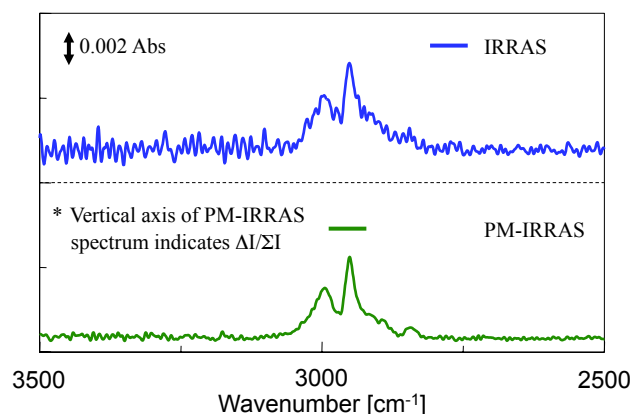


Fig. 2. Comparison between IRRAS spectrum and PM-IRRAS spectrum (normalized, offset plotting)

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## Instrument

The appearance of PM-IRRAS measurement system and system layout of polarization modulation unit are shown in Fig. 3. The incidence angle of polarized light of this specific system is  $85^\circ$ , while the optimal incidence angle in general is considered as  $80 \sim 89^\circ$  depending on the kinds of metal and wavenumber of incidence light. In addition, the whole system can be vacuumed. In principle PM-IRRAS can reduce the noise due to  $H_2O$  and  $CO_2$  but vacuum of whole optics can enhance the sensitivity further. Apart from this, the system is capable of blowing gas to sample or heating sample, enabling the system to be used for monitoring of film generation in process or structural changes in such film.

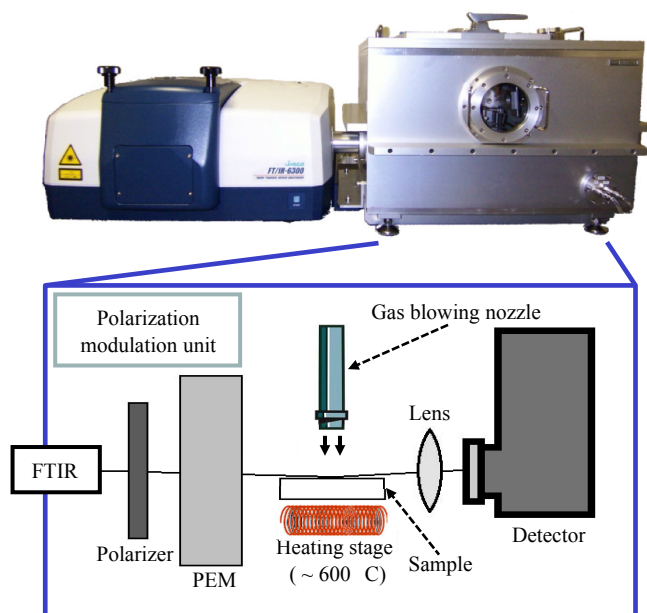


Fig. 3. Appearance of FT/IR-6300FV & Polarization modulation unit (upper)  
System layout of polarization modulation unit (lower)

## Measurement example

### 1. PMMA thin film on Al mirror

The measurement result of PMMA thin film on Al mirror is shown in Fig. 4. The obtained spectrum has good S/N without effect of  $H_2O$ .

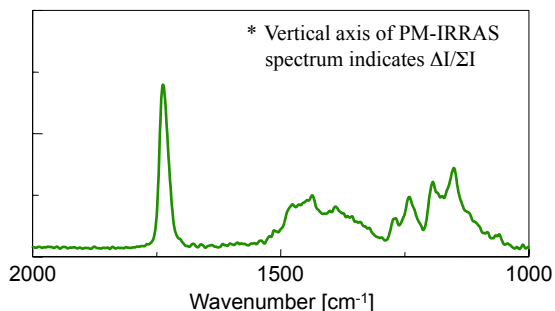


Fig. 4. Measured spectrum of PMMA thin film

#### [Measurement condition]

Instrument: FT/IR-6300FV & polarization modulation unit  
 Detector: MCT-N  
 Accumulation: 50  
 Resolution:  $4 \text{ cm}^{-1}$   
 PEM center wavenumber:  $1700 \text{ cm}^{-1}$

### 2. PMMA thin film on Al mirror

Measurement result of native oxidation film on Al mirror is shown in Fig.5. The thickness of the native oxidation film obtained using ellipsometer (JASCO: M-220) is  $46.9 \text{ \AA}$  and it is confirmed that the measurement of thickness in  $\text{\AA}$  level was implemented in about 1 minute time utilizing PM-IRRAS.

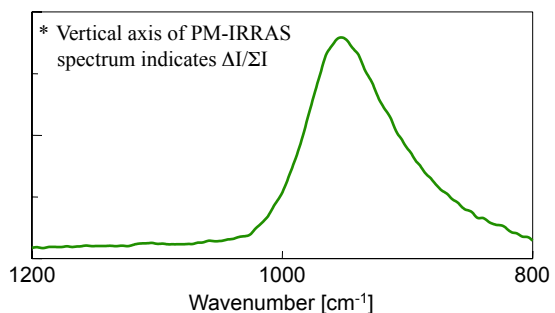


Fig. 5. Measured spectrum of native oxide film on Al mirror

#### [Measurement condition]

Instrument: FT/IR-6300FV + Polarization modulation unit  
 Detector: MCT-N  
 Accumulation: 100  
 Resolution:  $4 \text{ cm}^{-1}$   
 PEM center wavenumber:  $1000 \text{ cm}^{-1}$