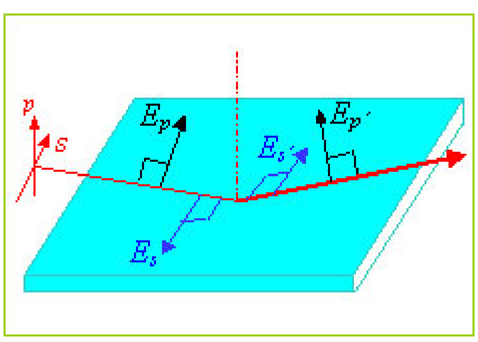
What is PM-IRRAS?

Polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) is used for characterization of thin films or monolayer on metal substrate, because it has advantage of high surface sensitivity, and of the surface selection rule. In addition, the advantage over the conventional IRRAS mode is that modulated reflectivity is independent on the isotropic adsorption from gas or bulk water. Consequently the interfering effect of water vapor and carbon oxide can fairly be eliminated.

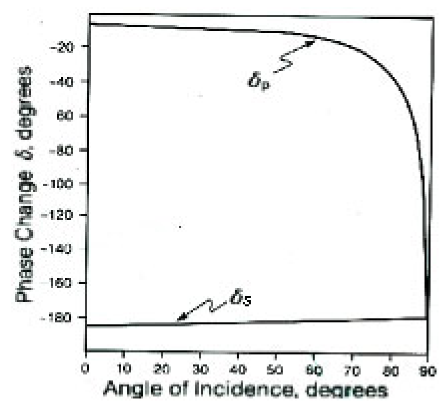
The IRRAS is dependent upon the optical constants of the thin film and substrate, the angle of incidence, as well as the polarization of the incident IR radiation. A photo-elastic modulator generates alternating linear states of polarized light. Fig.(a) shows the incident and reflected electric vectors of the so-called *p* and *s*components of radiation where *p* refers to parallel polarized radiation and *s* to perpendicular polarized radiation with respect to the plan of incidence. The phase shift of the perpendicular component, *s*, exhibits no significant dependence upon the variation of the angle of incidence (as shown in Fig.(b)). Because the phase shift of the perpendicular component, *s*, is nearly 180° for all the angles of incidence, the net amplitude of the IR radiation parallel to the substrate surface is zero. In contrast, the phase shift of the parallel component, *p*, strongly depends upon the angle of incidence. The *p*-polarized component goes through a maximum at 88°. At such grazing incidence, the *p*-polarized radiation sums up ofE_p and $E_{p'}$, leading to a net combined amplitude that is almost twice that of the incident radiation. This feature is utilized to obtain the differential reflectance spectrum of the adsorbed surface species, $\Delta R/R$, which is expressed as follows:

$$\Delta R/R = (I_p - I_s)/(I_p + I_s)$$

Where I_p is the intensity of *p*-polarized component of radiation, and I_s is the intensity of *s*-polarized component of radiation.



(a) Schematic illustration of the *p* and*s* polarization radiation



(b) Variation of phase change in the*p*-component and *s*-component radiations as function of the angel of incidence

Only *p*-component radiation interacts with the surface of sample. Consequently, the active vibrations that can be detected in IRRAS must have a component of the dynamic dipole polarized in the direction normal to the surface of sample. These results give the so-called “surface selection rule” for PM-IRRAS. The “surface selection rule” is used to study the molecular orientation of thin films or monolayers deposited on metal or dielectric substrates.

The PM-IRRAS measurement can be summarized as follows:

Maximum spectral intensity will be detected when the angle of incidence is near grazing incidence (*ca.*~80°)

Only the parallel component of the incident radiation is adsorbed by the adsorbed molecules on the metal substrate.

The dipole transition moment of the adsorbed molecules must have a component orientated along the surface normal in order to adsorb the IR incident radiation.

The adsorption of the parallel component of the incident radiation is directly proportional to the film thickness when the film is thin enough (<10nm).

More details of PM-IRRAS measurement can be found in the listed references.

References:

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