SHIMADZU APPLICATION NEWS

LA103-E005

● SPECTROPHOTOMETRIC ANALYSIS

No.A325

Measurement of layer-by-layer self-assembly film using RAS-8000 grazing angle specular reflectance accessory

Decent spectra cannot be obtained if thin films such as organic LB films are measured using a reflector with a small angle of incidence. This type of measurement however becomes possible if a grazing angle specular reflectance accessory is used. Introduced here is an example of thin film measurement using layer-by-layer self-assembly film to illustrate the effect of different incident angles on the spectrum.

■ Layer-by-layer self-assembly film

Layer-by-layer self-assembly films are films on which a positively charged polymer and a negatively charged polymer are alternately accumulated on a substrate. Bio-sensors are its principal example of application. This sensor can be used to obtain the substrate concentration, and is particularly employed in the fields of food and pharmaceutical products for quality control purposes. The layer-by-layer self-assembly film used here is a sample that consists of polyallylamine (PAA) as the positively charged polymer, and polyvinyl sulfate (PVS) as the negatively charged polymer. The film was made by alternately accumulating PAA and PVS after the vapor deposition of gold on a glass substrate, and at the end 5% of the amino group of the PAA layer laid on as the uppermost surface was substituted with azobenzene carboxylic acid amide (Az).

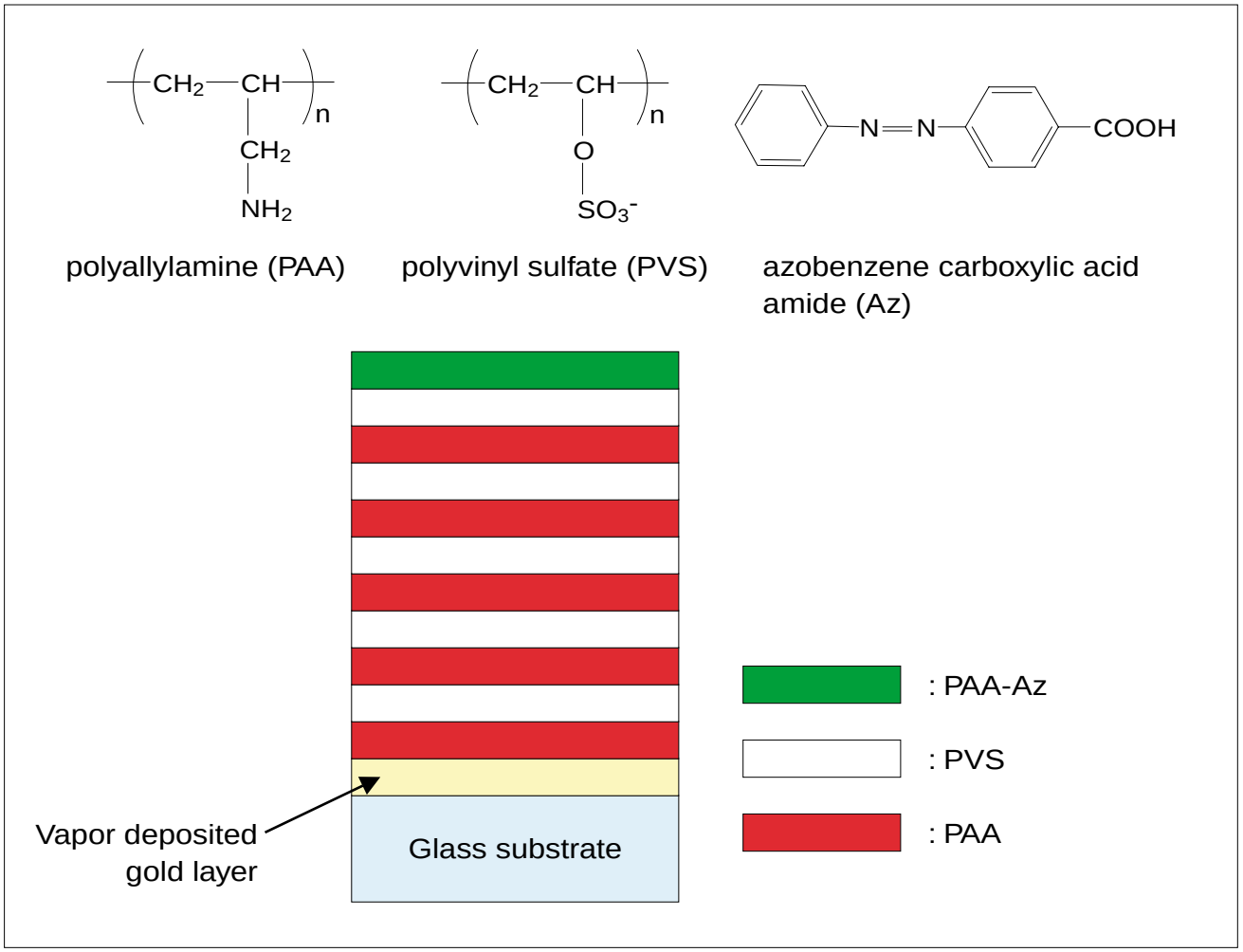

Fig.1 Structure of layer-by-layer self assembly film and composition of each layer

■ Spectra of layer-by-layer self-assembly film

Fig.2 shows the spectrum of the layer-by-layer self-assembly film measured at an incident angle of 70° using a grazing angle specular reflectance accessory. The measurement conditions are shown in Table 1.

Table 1 Measurement conditions

Resolution	:	4.0cm^{-1}
Accumulation	:	500times
Detector	:	DLATGS

Peaks arising from S=O can be seen clearly around 1100cm^{-1}, while peaks due to the amide bonds can be clearly seen around 1550 and 1650cm^{-1}.
Fig.3 superimposes the spectra of the layer-by-layer self-assembly film measured at an incident angle of 75° using a grazing angle specular reflectance accessory onto the spectrum in Fig.2. The green line is for the incident angle of 70° and the red line is for the incident angle of 75°.
Looking at Fig.3, it is evident that the peak intensity increases as the incident angle becomes greater.
So far the effect of the incident angle on the spectrum peak intensity has been illustrated: now an example where the peak intensity is increased even further by combining the use of a grid polarizer shall be introduced.
When polarized light is incident on a thin film formed on a metallic substrate, a phase change will occur at the metallic surface. When this happens, the polarized light vectors of the vertically polarized light each end up facing the opposite direction, and as such will not be reflected in the absorption peak, whereas the horizontally polarized light will generate a vertical standing wave with respect to the substrate. The peak intensity will therefore increase even further by using just the horizontally polarized light through the usage of a grid polarizer in combination.
Fig.4 shows the spectra of the layer-by-layer self-assembly film measured at an incident angle of 75° using a grazing angle specular reflectance accessory. The red line shows the spectrum without the polarizer, and the blue line shows the spectrum obtained with the polarizer.
Looking at Fig. 4, it is clear that the peak intensity has become extremely strong with the use of the polarizer. However, attention needs to be paid to the fact that the light quantity is reduced by the employment of the polarizer, which results in a lowered S/N ratio.
In this way, the intensity of the peak obtained will increase as the incident angle is made greater, and moreover will increase even further by using a polarizer.
Although not described here, accessory devices with incident angles of 80° and 85° are available as well. Incidentally, thin films of approx. 20Å can be measured using the 85° accessory devices.

As a final note, the sample used to prepare this application news has been kindly supplied by Dr. Junichi Anzai, Professor from the faculty of pharmaceutical sciences at Tohoku University. Thank you very much for your assistance.

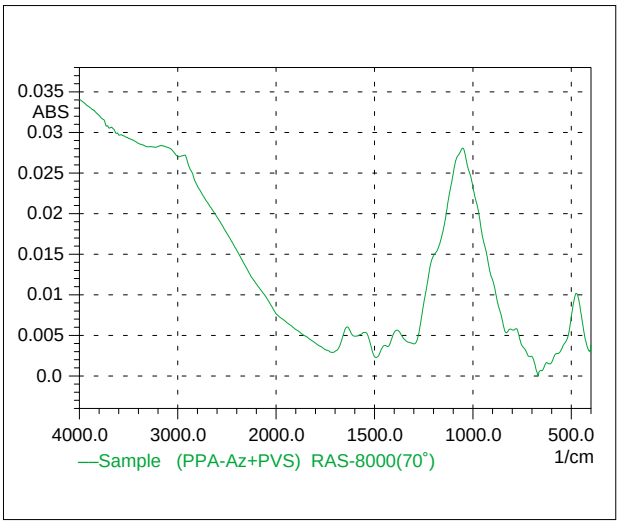

Fig.2 Spectrum of layer-by-layer self assembly film

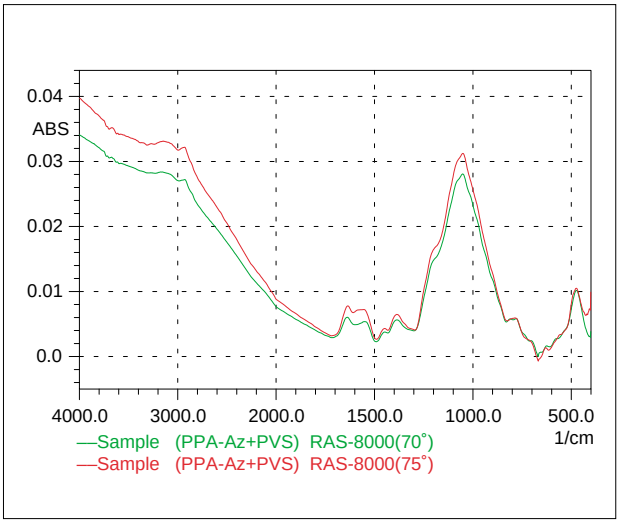

Fig.3 Spectra of layer-by-layer self-assembly film measured with different incident angles

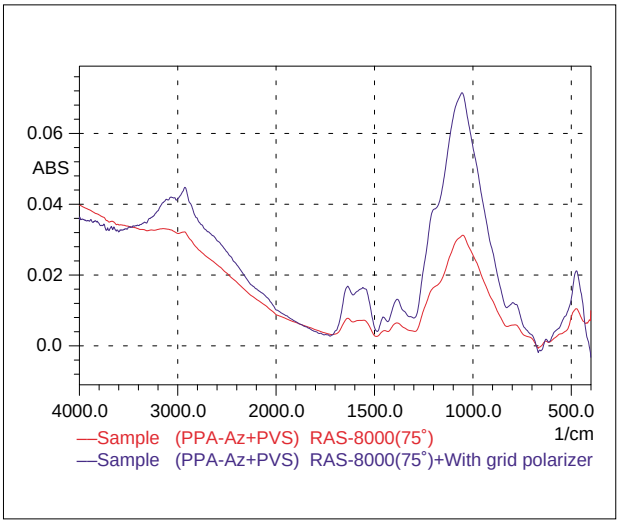

Fig.4 Influence of the polarizer on the spectra of layer-by-layer self-assembly film

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