

Intensity Enhancement of the Infrared Transmission Spectra of *p*-Nitrobenzoic Acid by the Presence of the Pb Films

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Infrared transmission spectra of *p*-nitrobenzoic acid deposited on a Pb film evaporated on a KBr substrate were measured in the Pb film thickness region 0 to 150 nm. The enhancement of the infrared spectrum with the use of the Pb film was first observed. The dependence of the enhancement factor on the Pb film thickness was peculiar, and was discussed together with the structure of the Pb films to clarify the mechanism.

Recently, surface-enhanced infrared spectra of molecules adsorbed on Ag films have been reported by using attenuated-total-reflection (ATR) measurement,^{1,2} reflection measurement³ and transmission measurement.⁴⁻⁶ These enhancement phenomena have been interpreted due to the electromagnetic field effect on the surface of the thin Ag film; it becomes stronger when the film consists of Ag islands and/or when the film involves holes.^{1,6-8} This mechanism can account for characteristics of the enhancement although other mechanisms are also suggested: a mechanism⁹ based on the diffuse reflection of the infrared light at the surface made up of the Ag islands, and a mechanism¹ based on an increase in absorption coefficient caused by the chemisorption. Thus, the metal islands play important roles in the enhancement of the infrared spectra, considering that the chemical mechanism is still unclear.^{1,6,7} In the present paper, we report the enhancement of the infrared transmission spectrum of *p*-nitrobenzoic acid (PNBA) deposited on a Pb film evaporated on a KBr substrate in the Pb film thickness region of 0 to 150 nm. The intensity dependence of a band in the spectra on the Pb film thickness was very different from that with the use of the hitherto investigated metal films^{6,9} other than Pb. The characteristics of this intensity dependence were analyzed on the basis of the X-ray photoelectron spectroscopy (XPS) analyses of the Pb films, and the participation of Pb islands in this enhancement was discussed. This is the first observation of the enhancement of the infrared spectrum with the use of the Pb film.

The KBr substrate (Wako Pure Chemical Industries, Ltd.) in the form of cubic with a side 6.5 mm long was polished with a 3- μ m-grain-size abrasive. The Pb film was evaporated on the KBr substrate from a tungsten boat at about 1×10^{-5} Torr. The film thickness was monitored by a quartz thickness gauge (ANELVA EVM-32B). The deposition rate was kept at 0.075 nm/s within an accuracy of $\pm 30\%$. PNBA was dissolved into chloroform and 10 μ l of this solution was dropped onto the surface, and then the chloroform was volatilized in air. The infrared transmission spectra were recorded on the Fourier transform infrared spectrometer (Shimadzu FTIR-4200) at a spectral resolution of 8 cm^{-1} . The XPS studies were carried out in an ESCA-1000 (Shimadzu) electron spectrometer.

The infrared transmission spectra of PNBA (46 ng) deposited on the Pb films in the thickness region of 0 to 150 nm were measured, and some of them are shown in Figure 1. The

transmitted light was too weak to detect it at the thickness above 150 nm. Above 15 nm in thickness, the $\nu(\text{C=O})$ band at 1692 cm^{-1} disappeared, and moreover, new two bands appeared at around 1390 and 1570 cm^{-1} which are assigned to a symmetric stretching mode of carboxylate ($\nu_s(\text{COO}^-)$) and an antisymmetric one ($\nu_{as}(\text{COO}^-)$), respectively. These results suggest that PNBA dissociates the proton to generate *p*-nitrobenzoate on the Pb films as well as on the Ag films.⁶ The intensities of the bands in the spectra increased with increasing the Pb film thickness as shown in Figure 1. Therefore, the infrared transmission spectrum of PNBA was surely enhanced by the presence of the Pb film. The enhancement factor (ratio of the absorbance measured with and without Pb, respectively) had a maximum of 75 at 75 nm in thickness. So far, the enhancements of the infrared spectra have been observed with the use of Au, Cu, In, Ni, Pd and Pt films⁹⁻¹¹ as well as with the use of Ag,¹⁻⁶ but this is the first observation of the enhancement of the infrared spectrum with the use of the Pb film.

Figure 2 shows the plot of the intensity of the infrared spectra versus the Pb film thickness for the $\nu_s(\text{NOO})$ band. As the Pb film thickness is increased, the intensity increases to have a maximum at 75 nm and then keep a comparable value with the

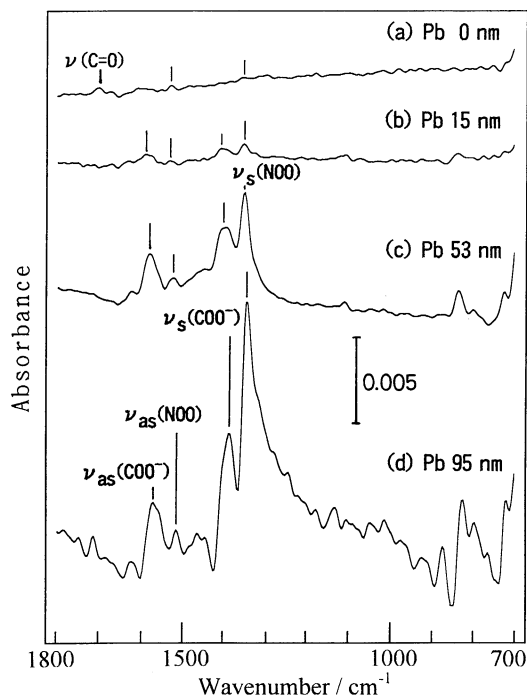


Figure 1. Infrared transmission spectra of PNBA (46 ng) deposited on the Pb films evaporated on the KBr substrates.

maximal value above 75 nm in thickness. This intensity dependence on the thickness is very different from that with the use of the hitherto investigated metal films^{6,9} other than Pb. Thus far, the intensity dependence on the metal film thickness has been investigated in detail for the transmission spectra with the use of the Ag film by Osawa et al.⁶ and for the ATR spectra with the use of the Ni, Pd and Pt films by Nakao et al.,⁹ respectively: the intensities of bands in the infrared spectra increase and then decrease rapidly through a maximum. Further, the thickness at which the maximum is observed is below 30 nm, depending mainly on the evaporated metal and the substrate.^{6,9} Especially, using the same transmission measurement of PNBA as the present work, the maximum is observed at 10 nm in thickness for the Ag film evaporated on the CaF₂ substrate.⁶ The mechanism of the enhancement with the use of the hitherto investigated metal films other than Pb is as follows: the electromagnetic field on the thin metal film becomes stronger, and this enhanced electromagnetic field causes the enhancements of the infrared spectra.^{1,3,6} In this mechanism, metal islands which constitute the metal film play important roles in the enhancement of the electromagnetic field.^{1,6} Actually the thin metal films less than about 10 nm thickness consist of the metal islands,³ and a little thicker (about 30 nm) metal films involve some holes which can institute for the metal islands,⁸ and hence the rapid decrease through a maximum at the film thickness less than 30 nm is interpreted on the basis of the continuous film.¹ This mechanism,^{1,6} however, is not thought to explain the enhancement with the use of the Pb film because the following reasons: the thickness of 150 nm up to which the enhancement was observed is much larger than 30 nm, and such an intensity decrease as is observed with the use of the hitherto investigated metal films^{6,9} was not observed with the use of the Pb film. To make sure this prediction, it is necessary to study the structure of the Pb film.

XPS analyses of the Pb films evaporated on the KBr substrates were carried out after ion sputtering with Ar⁺ for 2 min and 0 min, and the intensity dependence on the Pb film thickness for the Br 3d peak due to the KBr substrate is shown in Figure 3. The detection of the Br 3d photoelectrons means the exposure of the KBr substrate, considering that the Pb film is thicker than the mean free path of the photoelectrons (in general a few nm), and no detection of them means either that the Pb film is continuous or that the holes involved in the film are too small for the photoelectrons to pass through the holes from the KBr substrate. In the thickness region less than 95 nm, the intensity of the Br 3d peak is large and rapidly decreases with increasing the Pb film thickness, and increases with increasing

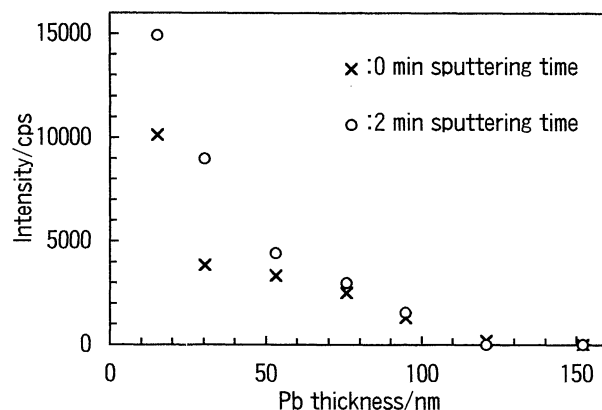


Figure 3. Intensity dependence of the Br 3d peak of the XP spectra of the Pb film evaporated on the KBr substrates on the Pb film thickness.

the sputtering time. These results suggest that the Pb film less than 95 nm in thickness has an island structure. Above 122 nm in thickness, the intensity is 0 cps at the sputtering time of both 2 min and 0 min, which suggests the Pb film is nearly continuous. Thus, the Pb film varies from the film made up of the Pb islands to the nearly continuous film with increasing the thickness. On the other hand, little change in the intensity of the $\nu_s(\text{NOO})$ band was observed in the 75-150 nm region in contrast with the large structural changes of the Pb film, that is, the magnitude of the enhancement is almost independent of the structure of the Pb film in the 75-150 nm region. This suggests that this enhancement is hardly related to the Pb islands although the participation of the very small holes described above in this enhancement is necessary to be further investigated by using other measurements such as the atomic force microscopy. Nakao et al.⁹ suggested a mechanism based on the light scattering or diffuse reflection at the interface of the metal islands for the enhancements with the use of the Ni, Pd and Pt films. This mechanism cannot account for the enhancement with the use of the Pb film because this mechanism is also based on the island structure of those metal films. An increase in absorption coefficient caused by the chemisorption of the molecules was suggested to provide an enhancement, but this chemical mechanism is still unclear.¹ Extensive data on enhancements of some molecules other than PNBA and on properties of the Pb films are necessary for further explanation of the enhancement with the use of the Pb film.

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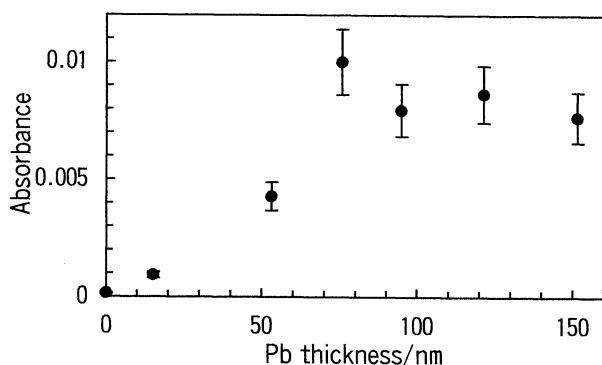


Figure 2. Intensity dependence of the $\nu_s(\text{NOO})$ band of PNBA (46 ng) on the Pb film thickness.

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