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FAR-INFRARED SPECTRA OF AsF_5 DOPED $(CH)_x$

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Far-infrared spectra were measured with the AsF_5 doped polyacetylene films in order to understand the electrical conduction mechanism. From the reflection data, the mechanism of the insulator-metal transition is discussed. That is, the intermediately doped film consists of small metallic particles and the highest doped film becomes the homogeneous metal, while the soliton model may be supported for the light doping.

Polyacetylene, $(CH)_x$, is one of the simplest of the conjugated organic polymers and is well known to be a large band gap semiconductor. However, Shirakawa *et al.*[1)] have shown that this polymer undergoes dramatic increases in electrical conductivity upon exposure to vapors of chlorine, bromine, iodine, or arsenic pentafluoride (AsF_5). These experiments suggested that the material passes from an insulating to a metallic state and several mechanisms of the conductivity increase were proposed. These include the Mott transition among localized carriers,[2)] the soliton mechanism,[3)] and the percolation transition.[4)]

Hoffman *et al.*[5)] made far-infrared transmission measurements on iodine doped *trans*-$(CH)_x$ in an attempt to decide which mechanism is true. However, they got the linear frequency dependence of the absorption coefficient although the frequency dependence of the absorption coefficient of the free carrier band in the far-infrared region is known to be the square root for the Drude model and quadratic for the small metal particle composites.[6)] Therefore, we intended far-infrared reflection measurements of AsF_5 doped $(CH)_x$ in order to explore the mechanism of the conductivity increse.

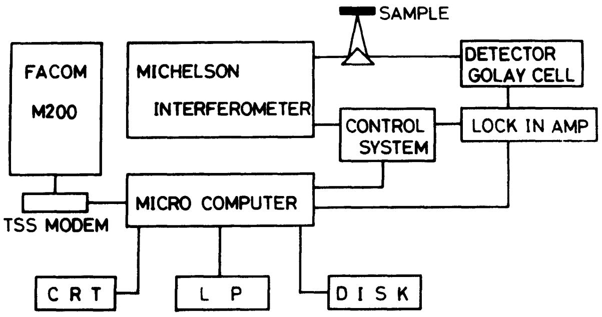

Fig.1 Scheme for FIR measurement.

The *cis*-rich polyacetylene films were prepared from acetylene gas by treatment of the Ziegler-Natta catalyst in hexane at -80 °C as described by Shirakawa and coworkers.[7)] The films were doped in the vessel for the FIR measurement by exposure to the vapor of AsF_5 at room temperature.

The FIR measurements were made according to the scheme shown in Fig.1. An ADKIN Far Infrared Michelson Interferometer

Model FIRMI was employed as the interferometer. The Golay cell was used as the detector and the beam splitter was Toray-Lumirror of thickness 16 μm. The interferogram was recorded at multiples of 4 μm in the optical path difference. During this time, the output of the detector, suitably amplified and synchronously rectified, was fed into a NEC PC8801 personal computer through an analog-to-digital (A/D) converter, and was stored into the 8 in. floppy disk. The Fourier transformation was computed with a FACOM M200 computer in the Computer Center of Nagoya University. The obtained spectra were monitored and printed out by the line printer connecting with the PC8801 computer.

Pure $(CH)_x$ film has a strong $\pi\rightarrow\pi^*$ band in the 19000 cm^{-1} region. However, on doping $(CH)_x$ with AsF_5, the broad absorption band having a peak at 6000 cm^{-1} is observed over the wide region from 300- to 25000-cm^{-1}, while the $\pi\rightarrow\pi^*$ band at 19000 cm^{-1} disappears.[8] This spectral change means that doping produces the free carriers and that the broad band may be assigned to the free carrier absorption. The FIR, IR, and visible reflection spectra for a series of the AsF_5 doped samples are shown in Fig.2. In order to discuss the frequency dependence of reflection spectra, the dielectric function, $\langle\varepsilon(\omega)\rangle$, of the doped films can be expressed according to the Maxwell-Garnett model,[6]

$$\langle\varepsilon(\omega)\rangle = 1 + \frac{\alpha f(\varepsilon(\omega) - 1)}{1 + g(1 - \alpha f)(\varepsilon(\omega) - 1)} \equiv \langle\varepsilon_1(\omega)\rangle + i\langle\varepsilon_2\ \omega\ \rangle$$

where f is the filling factor of the metallic region in the doped $(CH)_x$ film, α is the fractional alignment factor, and g is the typical depolarization factor. $\varepsilon(\omega)$ is the simple Drude dielectric constant as defined in the following equation,

$$\varepsilon(\omega) = \varepsilon_{core} - \frac{\omega_p^{\ 2}}{\omega^2 + i\gamma\omega} \equiv \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

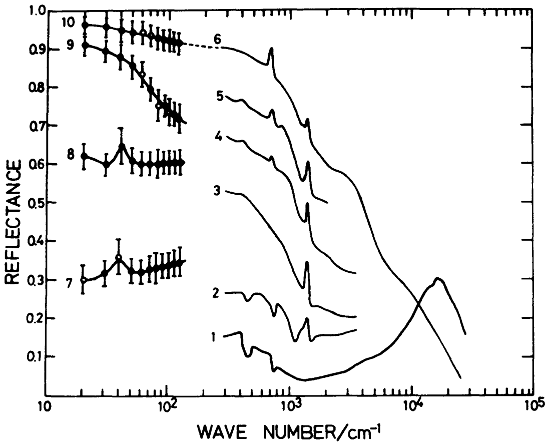

Fig.2 Observed reflection spectra for a series of thick $(CH)_x$ films doped with AsF_5,

1. pure, 2. $\sigma \simeq$ 20 S/cm,
3. $\sigma \simeq$ 30 S/cm, 4. $\sigma \simeq$ 120 S/cm,
5. $\sigma \simeq$ 500 S/cm, 6. $\sigma \simeq$ 1000 S/cm,
7. $\sigma \simeq$ 25 S/cm, 8. $\sigma \simeq$ 100 S/cm,
9. $\sigma \simeq$ 400 S/cm, 10. $\sigma \simeq$ 1000 S/cm.

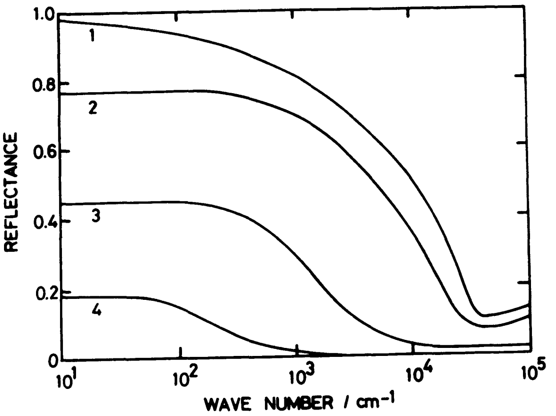

Fig.3 Calculated reflection spectral change due to the various concentration of free carriers,

1. $N = 2.0 \times 10^{22}\ cm^{-3}$,
2. $N = 1.6 \times 10^{22}\ cm^{-3}$,
3. $N = 4.0 \times 10^{21}\ cm^{-3}$,
4. $N = 1.0 \times 10^{21}\ cm^{-3}$.

Here, $\omega_p = (4\pi Ne^2/m^*)^{1/2}$ is the plasma frequency of the free carrier, γ is the band width, m^* is the effective electron mass, and N is the number density of the free carriers in the doped $(CH)_x$ film. Then, the reflectivity of the film is given as follows,

$$R(\omega) = \frac{1 + |\langle\varepsilon(\omega)\rangle| - \sqrt{2(|\langle\varepsilon(\omega)\rangle| + \langle\varepsilon_1(\omega)\rangle)}}{1 + |\langle\varepsilon(\omega)\rangle| + \sqrt{2(|\langle\varepsilon(\omega)\rangle| + \langle\varepsilon_1(\omega)\rangle)}}$$

and

$$|\langle\varepsilon(\omega)\rangle| = (\langle\varepsilon_1(\omega)\rangle^2 + \langle\varepsilon_2(\omega)\rangle^2)^{1/2}$$

In the heavily AsF_5 doped film ($\sigma \simeq 10^3$ S/cm), the observed reflection spectrum behaves like the homogeneous metal as is shown in Fig.2 (curve 6), and the calculation of the best fit between the observed (curve 6) and calculated spectra gave $\hbar\omega_p = 37450\ cm^{-1}$, $\gamma = 18700\ cm^{-1}$, and $\varepsilon_{core} = 5.13$ by using the simple Drude dielectric function.[9] Then, the change of reflection spectra with increasing the concentration of free carrier is simulated as shown in Fig.3, where the parameters γ and ε_{core} are fixed but only ω_p is varied with N. Furthermore, the filling factor, f, is defined to be the ratio (N/N_π) of the number density of the free carrier (N) and the total π-electron ($N_\pi \simeq 2 \times 10^{22}\ cm^{-3}$). α and g are taken to be 1 and 0.01, respectively.

The calculated reflection spectra are in satisfactory agreement with the observed ones (Fig.2). That is, the reflectivity increases over a wide region from 30- to $15000\text{-}cm^{-1}$ with increasing the dopant concentration. However, the reflectivity for the lightly doped films approaches a value smaller than unity with decreasing frequency although it reaches unity for the heavily doped film ($\sigma \simeq 10^3$ S/cm) as is predicted in the Drude model. This fact means that the lightly doped system ($f < 1$) consists of the small metal particles which do not contact each other and the heavily doped film ($f \simeq 1$) becomes the homogeneous metal. On the other hand, it has been reported that the measurements of the magnetic susceptibility[10] and the visible and infrared absorption[11] support the soliton mechanism. Accordingly, the following mechanism may be proposed in order to explain the above-mentioned behavior.

The light doping forms the spinless charged solitons on the $(CH)_x$ chain ($y < 0.01$, $\sigma \leqq 1$ S/cm). The further doping ($0.01 < y < 0.05$, $1 \leqq \sigma \leqq 500$ S/cm) makes a small region of metallic $(CH)_x$ fibrils. In this dopant concentration, the doping remains inhomogeneous and the $(CH)_x$ films consist of metallic regions separated by undoped regions. The model of such inhomogeneity or barriers between $(CH)_x$ fibrils is in good agreement with the hopping mechanism proposed by the temperature dependence of the electrical conductivity,[9,12]

$$\sigma = \sigma_0 \exp\{-(T_0/T)^{1/4}\}$$

For the highest doped sample of the electrical conductivity, $\sigma \simeq 10^3$ S/cm, the doping is homogeneous and the film becomes metallic over the whole region.

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