

Interference and electro-optical Kerr effects responsible for electroabsorption spectra of transparent Parylene-C films

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Abstract

Electroabsorption spectra of Parylene-C films are found to exhibit several peaks whose wavelengths depend on the thickness of the film. The spectral feature is well correlated to the first derivative of the transmission spectrum of the Parylene-C film sandwiched between two reflective metal layers, and the peak intensities are in proportion to the square of the magnitude of a modulation voltage. The electroabsorption spectra observed in a transparent region of the electrically insulating films are accounted for in terms of the interference effect coupled with the electro-optical Kerr effect of the Parylene-C films.

Keywords: Electroabsorption; Parylene; Interference effect; Electro-optical Kerr effect

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1. Introduction

Modulation spectroscopy deals with extremely small changes in absorption or reflectance spectra of a sample under a periodical modulation of a physical parameter by use of a phase-sensitive detection or a lock-in technique. In this spectroscopy, insignificant backgrounds can be eliminated by its derivative nature and sensitivity can be greatly enhanced in comparison with measurements of differences between absolute spectra. These characteristics of the modulation technique allow us to detect sensitively spectral features of organic films buried in normal spectra and the technique provides various sorts of valuable information on the sample. In particular, electroabsorption (EA) spectroscopy using electric field as a periodical perturbation has been employed to study charge-transfer excitations of organic molecules in the solid state [1-5]. The observed spectra have similarity to the first- or second-derivative of absorption spectra, depending on the nature of excited states of molecules. Friend et al. are the first to apply the EA technique to molecular films in Schottky diode and metal-insulator-semiconductor (MIS) diode structures. These authors have induced charged molecules at accumulation or inversion regions in molecular semiconductors by applying electric field and have successfully observed absorption spectra of charged states of organic molecules [6-9]. This modulation technique based on the generation of electric-field-induced charges has been used and now extended to characterize vibrational modes or spin states of charged molecules [10-12]. In view of a promising nature of molecular thin films as an active component in electronic and optoelectronic devices such as organic light-emitting-diodes (OLED), field-effect-transistors (FET), and solar cells, to get an insight into solid-state electronic properties of these molecular films based on the EA techniques is of great importance for developing excellent molecular-based (opto)electronic devices.

This Letter describes measurements of EA spectra of Parylene-C films which have been used as an insulating layer in organic FETs and for encapsulation of OLED because of its superior oxygen and water barrier properties [13-15]. In the literature, a few studies report unexpected

peaks in EA spectra of molecular films in the MIS diode structure [6,16,17]. This side effect (additional EA peaks) is tentatively ascribed to the interference effect due to a thin insulating film without a further investigation on its detailed mechanisms. The present study with cells comprising a transparent and insulating Parylene-C film alone reports EA spectra in the visible and the side effect observed earlier are explained on the basis of a combination of interference and electro-optical Kerr effects.

2. Experimental

Dichloroparacyclophane (diX-C) was obtained from Daisan Kasei Co., Ltd. Sandwich-type cells of glass/Al/Parylene-C/Au were fabricated by first evaporating aluminum directly onto a precleaned glass substrate at 10^{-4} Pa. Parylene-C films were deposited on it in a home-made reactor consisting of a quartz tube with three temperature zones. The diX-C was vaporized in the vaporization zone at 100°C , cleaved in the pyrolysis zone at 700°C , and polymerized at room temperature in the deposition zone where Al-coated glasses were placed. Finally, a gold film was evaporated over the Parylene-C film at 10^{-4} Pa. Nominal thicknesses of aluminum and gold layers were 10 and 25 nm, respectively. The active area of the Parylene-C film defined by the overlapped metal films was $3 \times 3 \text{ mm}^2$. EA signals ($-\Delta T/T$) were measured in the transmission mode using an EA spectrometer composed of a 150W tungsten halogen lamp, a monochromator (Shimadzu SPG-120), a Si photodiode (Hamamatsu Photonics S1226-5BK), a current-voltage amplifier (NF LI-76) and a lock-in amplifier (NF LI-5640). The a.c. modulation voltage oscillating between 0 and V_p was applied to the cell by amplifying the internal oscillator output of the lock-in amplifier using a piezo driver (Mess-Tek M-2633). The peak modulation voltage V_p was typically 1 to 100 V. The modulation frequency was the same as the reference frequency of the lock-in amplifier and in-phase signals were measured. Wavelength scanning and data acquisition from the lock-in amplifier were automatically made with a personal computer via I/O

port and RS232C interface. Transmission spectra of the sandwich-type cells were taken on a spectrophotometer (Shimadzu UV-3101PC). Thicknesses of Parylene-C films were evaluated from capacitances measured with an LCR meter (Hioki 3522) using a dielectric constant of 3.10 for the Parylene-C film.

3. Results and discussion

Fig. 1 depicts a typical EA spectrum of a Parylene-C film with a nominal thickness of 180 nm in the wavelength range of 350-850 nm, where the voltage was modulated at 200 Hz between 0 and 50 V with respect to the Al electrode. The sign of the applied voltage did not affect the shape and magnitude of the spectrum at all. Two sets of almost symmetrical signals centered at 420 and 640 nm are seen in the wavelength range where the polymer film is transparent, demonstrating strongly that the spectrum is not associated with optically excited states of the polymer. A small hump at 545 nm is ascribable to an uncompensated component due to an abnormal dispersion of the monochromator used. It is worthy to note here that the wavelength ratio of the two nodes, 640 and 420 nm, is 1.52 close to $3/2$. The spectral feature, especially wavelengths and the number of the nodes, varied depending on the film thickness, as shown in Fig. 2 for the 244-nm Parylene-C film. We find here that nodes at 428 and 584 nm do not depend upon the applied voltage ranging from 10 to 100 V and importantly the ratio of 584 to 428 nm is 1.36 close to $4/3$. The ratios of $3/2$ and $4/3$ which depend on the film thickness hint us that the modulation signals observed with Parylene-C films are related to the interference effect due to the transparent film sandwiched between two reflective metal films. To clarify this point, the transmission spectrum of the sandwich-type cell used in Fig. 2 was measured and is depicted in Fig. 3. The spectrum exhibits peaks at wavelengths close to 428 and 584 nm where the modulation spectrum exhibits nodes. This provides a further confirmation that an interference effect does take place in the present system like in the Fabry-Perot interferometer [6,16]. In a

previous EA study by Fichou et al. with sexithiophene (α -6T) as an organic semiconductor in the MIS device [17], they have observed two unclear bands in addition to the EA band of the radical cation (α -6T^{•+}). The former two bands shifted to the higher energy side by increasing the angle of the incident light. In view of this, these additional bands have been ascribed to optical interferences in the multi-layer MIS devices with poly acrylic acid or poly(methyl methacrylate) as a transparent insulating film. We note further that the first derivative of the transmission spectrum shown in the inset resembles in shape and position well the modulation spectrum of Fig. 2. On the other hand, the signal peak heights at 409.5, 450.5, 548.0, and 607.0 nm are plotted against the square of the field strength E in Fig. 4. These four plots fit excellently straight lines passing through the origin. Based on the above findings, one can explain the EA spectra observed with the Al/Parylene-C/Au cells as described below.

Given that the wavelength of the light in vacuum is λ and the refractive index of a dielectric film under application of an electric field E changes from n_0 at a zero field to n , the wavelengths of an incident light traveling through the film are λ/n and λ/n_0 for the film with and without the electric field, respectively. According to the change in the light wavelength within the film, when the transmission spectrum of the film at $E=0$ is $T(\lambda)$, the spectrum at E will be represented by the function $T(n_0\lambda/n)$ or $T\{n_0\lambda/(n_0+\Delta n)\}$ with $\Delta n=n-n_0$. Therefore, the difference of transmission spectra at electric fields of E and 0 is given by

$$\Delta T(\lambda) = T\{n_0\lambda/(n_0+\Delta n)\} - T(\lambda) \quad (1)$$

Since $\Delta n \ll n$, using a Taylor theorem one obtains

$$\begin{aligned} \Delta T(\lambda) &\approx -T'(\lambda)(\Delta n/n)\lambda \\ &\approx -T'(\lambda)(\Delta n/n_0)\lambda \end{aligned} \quad (2)$$

If the change of the refractive index is induced by the electro-optical Kerr effect [18], Δn can be expressed by

$$\Delta n = kE^2\lambda \quad (3)$$

where k is a Kerr constant of the dielectric film. Combining eqns. (2) and (3), one gets

$$\Delta T(\lambda) = -T'(\lambda)(k/n_0)E^2\lambda^2 \quad (4)$$

Consequently, the EA signal at λ is given by

$$-\Delta T(\lambda)/T(\lambda) = \{T'(\lambda)/T(\lambda)\}(k/n_0)E^2\lambda^2 \quad (5)$$

This expression explains a similarity between the EA spectrum of Fig. 2 and spectrum of $T'(\lambda)\lambda^2/T(\lambda)$ in the inset of Fig. 3, and the dependence of peak intensities of EA spectrum on E^2 as shown in Fig. 4.

On the other hand, the condition where the transmission spectrum shows peaks due to interference within the dielectric film of thickness d can be given by

$$\lambda_{\text{node}} = 2n_0d/N \quad (N = 1, 2, 3, \dots) \quad (6)$$

By referring to eqn. (5), it is clear that EA spectra have nodes at wavelengths of $2n_0d/N$. Based on eqn. (6), one can interpret that the node wavelengths of 640 and 420 nm observed in Fig. 1 correspond to $N=2$ and 3, and nodes at 584 and 428 nm in Fig. 2 correspond to $N=3$ and 4, respectively. It is to be noted here that the node wavelengths calculated with the n_0 value of 1.639 for Parylene-C, d values evaluated by the capacitance measurements, and appropriate N values are smaller than halves of the corresponding ones. The disagreement seems to be caused by underestimation of the film thicknesses due to surface roughness of the films. Taking into account of the roughness factor f_r of the Parylene-C film, eqn. (6) can be replaced by

$$\lambda_{\text{node}} = 2n_0d_{\text{cap}}f_r/N \quad (N = 1, 2, 3, \dots) \quad (7)$$

where d_{cap} is the film thickness evaluated by the capacitance measurement and thus $d_{\text{cap}}f_r$ denotes an average thickness of the dielectric film. In order to prove this relation, EA spectra with Parylene-C films of different thicknesses were measured and the observed λ_{node} values are plotted in Fig. 5 against $2n_0d_{\text{cap}}f_r$ with an assumption of $f_r=2.4$. It is seen that all the experimental points fit straight lines corresponding to the respective N values reasonably, demonstrating the validity for our interpretation of EA spectra of transparent Parylene-C films. A slight scattering of data

points is likely to arise from the difference in f_r for the respective Parylene films. Eqn. (5) with the data of Figs. 2 and 3 gives 0.17×10^{-12} cm V⁻¹ for the Kerr constant of Parylene-C. On the other hand, the longest λ_{node} value for an insulating layer of thickness d is $2n_0d$. This implies that a transparent insulating film used in the MIS diodes should be thinner than $\lambda/2n_0$ when the EA spectra are taken down to the wavelength λ . Otherwise, EA spectra of the MIS devices will be complicated by the side effect due to the optical interference and electro-optical Kerr effect.

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Figure captions

Fig. 1. EA spectrum of Al/Parylene-C(180 nm)/Au cell with a voltage modulation between 0 and 50 V at a frequency of 200 Hz.

Fig. 2. EA spectra of Al/Parylene-C(244 nm)/Au cell at a frequency of 200 Hz. Peak modulation voltages are changed from 10 to 100 V with an interval of 10 V.

Fig. 3. Transmission spectrum of the same cell as in Fig. 2. Curve in the inset is calculated by eqn. (5) with the transmission spectrum.

Fig. 4. Peak intensities in EA spectra of Fig. 2 plotted against the square of the electric field strength.

Fig. 5. Plots of λ_{node} vs. $2n_0d_{\text{cap}}f_r$ obtained with Al/Parylene-C/Au cells of different Parylene thicknesses, where EA spectra are measured in the wavelength range of 350-900 nm and the roughness factor f_r is assumed to be a common value of 2.4. Straight lines have slopes of $1/N$ with $N=1, 2, 3, 4,$ and 5 , and experimental points obtained with a sample cell are marked with the same symbol.

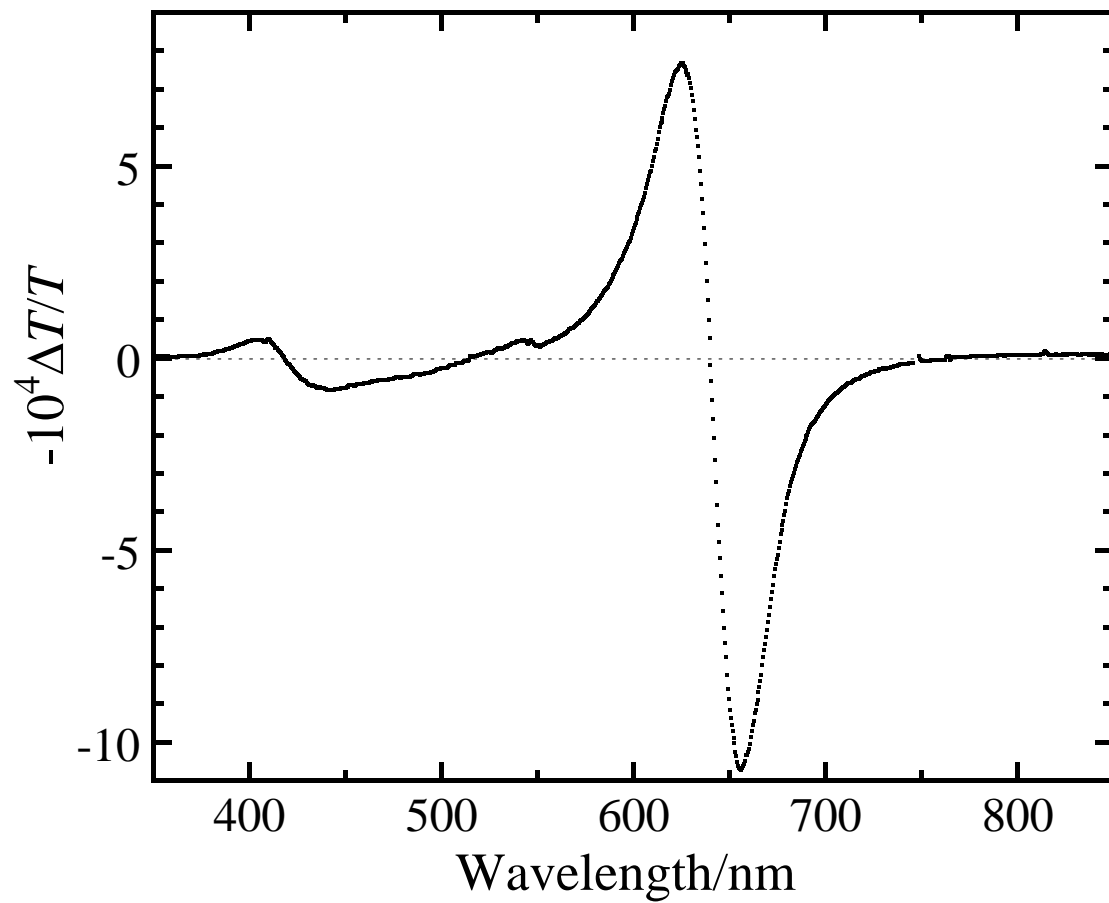


Fig. 1. Y. Harima et al.

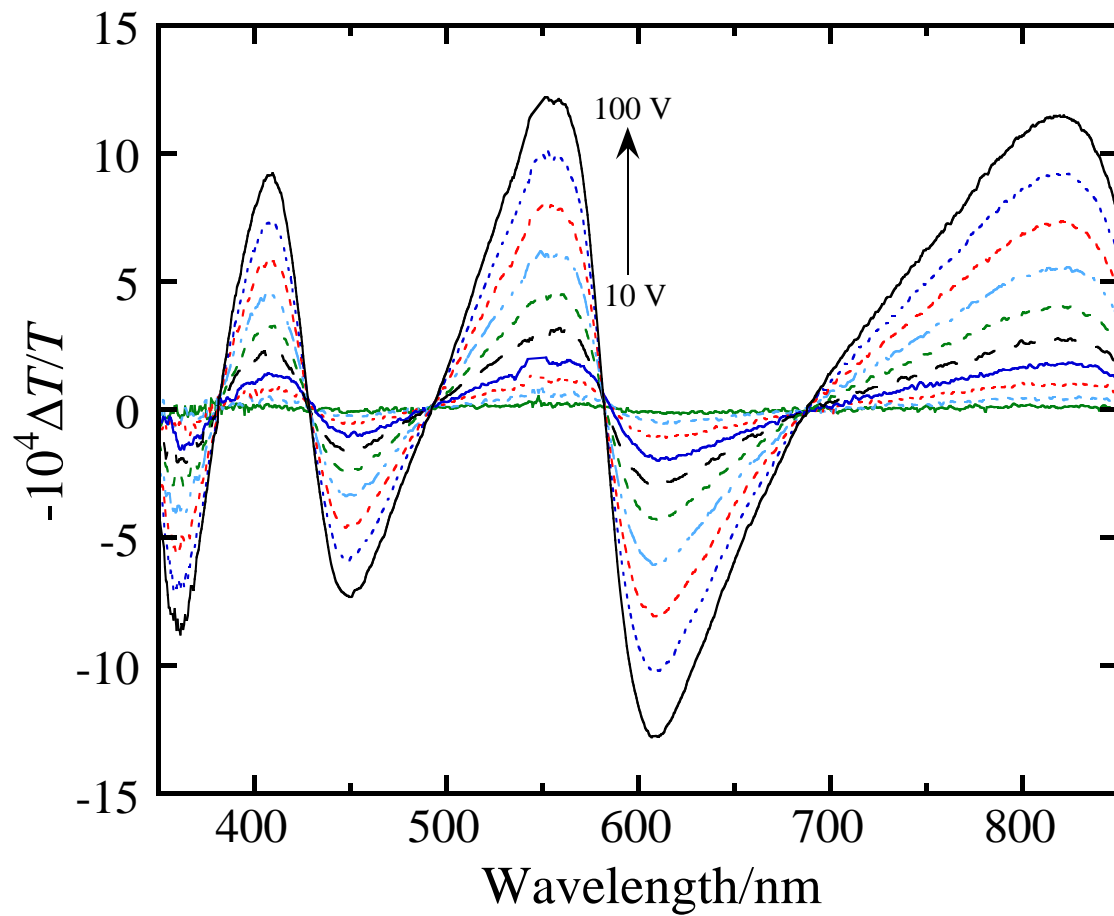


Fig. 2. Y. Harima et al.

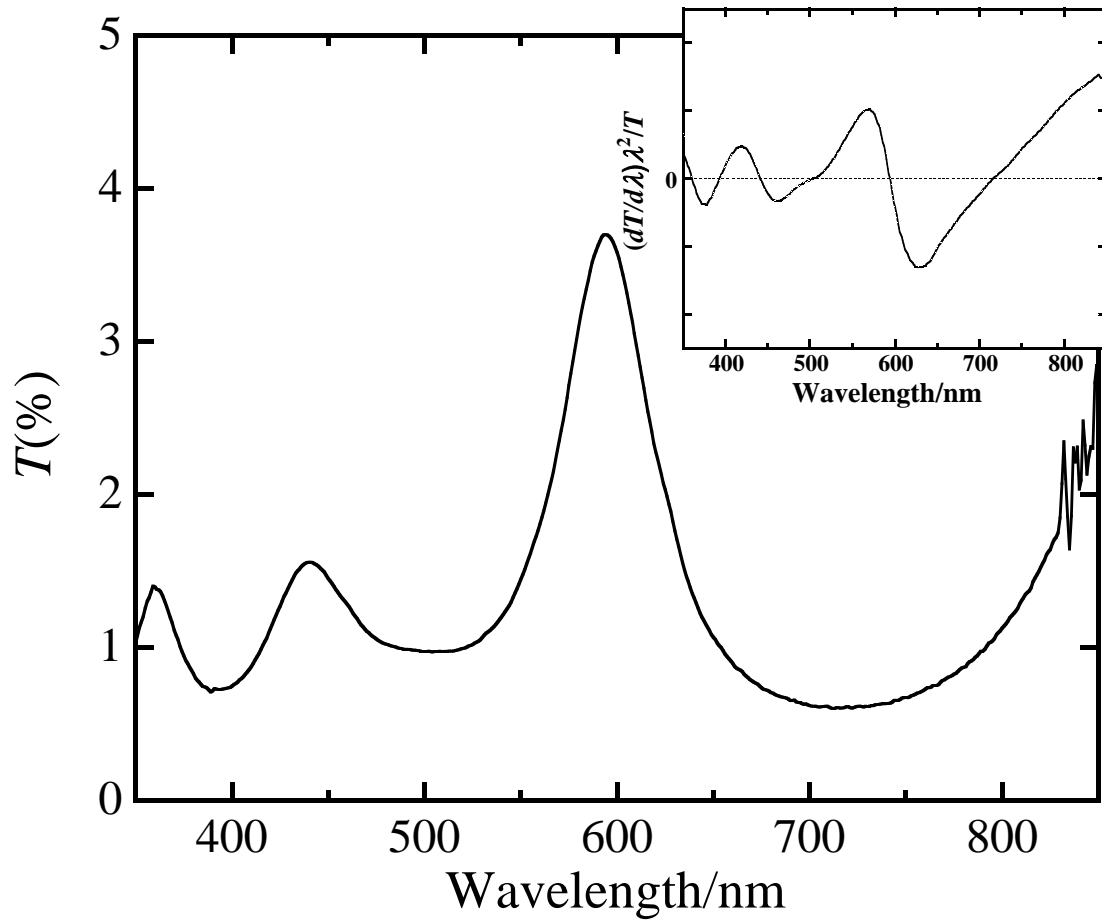


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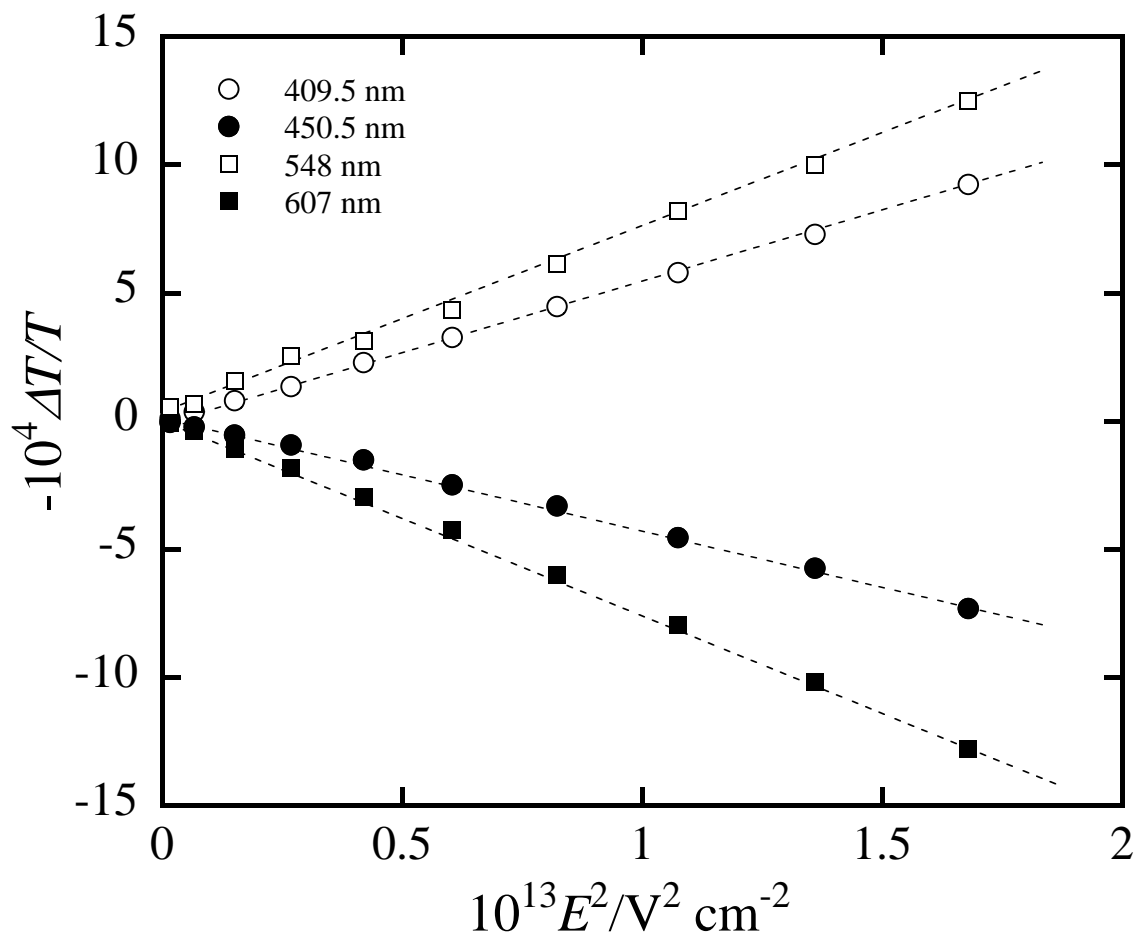


Fig. 4. Y. Harima et al.

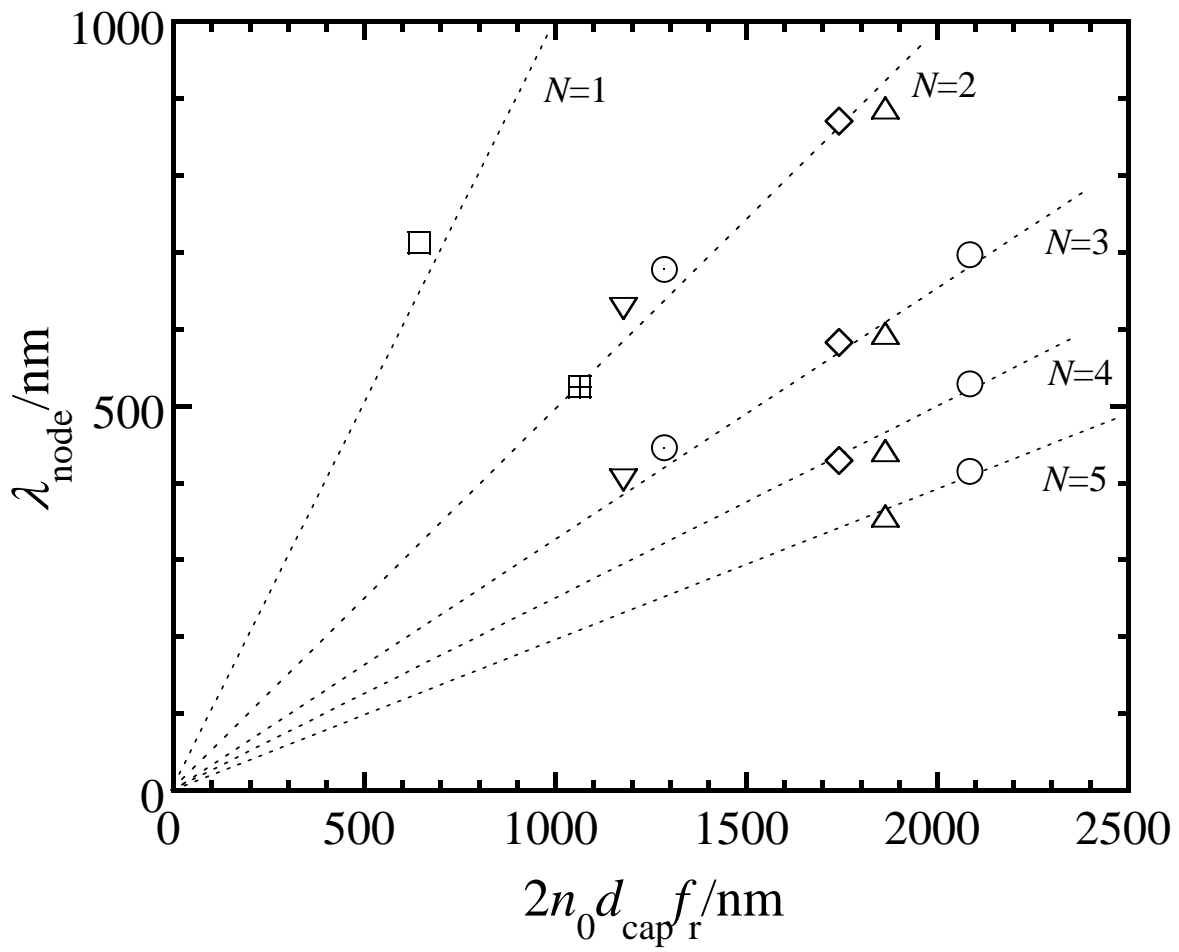


Fig. 5. Y. Harima et al.