

Dielectric properties of Au/C₆₀(OH)₂₄₋₂₆/Au structure

Y. Sun¹, S. Kanemitsu², K. Kirimoto³

¹Dept. of Electr. Engrg, Kyushu Inst. Techn., Kitakyushu, Japan

²Grad. School of Adv. Techn. Kinki Univ., Iizuka, Japan

³Dept. of Electrical and Electronic Engrg, Kitakyushu National College of Techn., Kitakyushu, Japan

Email address:

sun@ele.kyutech.ac.jp (Y. Sun)

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Abstract: Dielectric properties of the Au/C₆₀(OH)₂₄₋₂₆/Au structure were studied by measuring a.c. impedance and d.c. current in a wide temperature range. Three dielectric response characteristics were identified from Cole-Cole plots of a.c. impedance and dielectric dissipation factor of the structure. First, the bulk resistance and capacitance of the structure were observed at frequencies below 10 Hz, regardless of preparation condition of the Au electrode. Secondly, an interfacial characteristic of the Au foil/C₆₀(OH)₂₄₋₂₆ contact was observed as a peak of dielectric dissipation factor at frequency of 200 Hz. Thirdly, an interfacial characteristic of the Au paste/C₆₀(OH)₂₄₋₂₆ contact was also observed as a peak of dielectric dissipation factor at frequency of 1.7×10^5 Hz.

Keywords: Fullerenol, Fullerenol/Au Interface, Dielectric Property, Cole-Cole Plot, Dielectric Dissipation Factor

1. Introduction

Hydroxylated fullerenes, so-called fullerenols, C₆₀(OH)_n, synthesized for the first time twelve years ago [1, 2] are highly water-soluble fullerene derivatives. They have attracted much attention of researchers due to their outstanding physical and chemical properties. These derivatives have been used not only in medical and bio-applications [3-5] but also in dielectric [6], piezoelectric [7], and proton conducting and optical materials [8, 9].

In order to realize the practical use of the compound in the field of electronic devices, the fabrication of fullerenol films and the characterization of the fullerenol/metal interface are essential. Recently, fullerenol films have been deposited on glass and polymeric substrates by the method of drop and evaporation [10]. The results have indicated that electrical properties of the polymer/fullerenol junction can be improved by reducing the number of the OH groups and by implementing highly organized structures of molecules at the interface. Also, it has been reported that conductive properties of fullerenol materials were more ionic than electronic and depended on the amount of the OH groups [8].

In previous works [11], we have reported that Schottky barrier of the C₆₀(OH)₁₀/Au contact was 0.70 ± 0.02 eV and no significant effect of the applied electric field was

observed on the barrier height.

In the present study, we have characterized dielectric properties of the Au/C₆₀(OH)₂₄₋₂₆/Au structure by measuring a.c. impedance and d.c. current at various temperatures. Three dielectric response characteristics of the Au/C₆₀(OH)₂₄₋₂₆ contact were confirmed by analyzing Cole-Cole plots of a.c. impedance and dielectric dissipation factor of the structure.

2. Experimental

The Au/fullerenol/Au structure was prepared using C₆₀(OH)₂₄₋₂₆ powder (purity > 99 at.%) purchased from Nano-C (nanostructured carbon) Inc.. The OH groups were distributed on the surface of the C₆₀ molecule at random. The C₆₀(OH)₂₄₋₂₆ powder was pressed into a pellet at room temperature for waiting time of 50 min at 350 MPa. The formed pellet samples were 5 mm in diameter and 0.50 mm in thickness. The Au foil in thickness of 0.1 mm and gold particle paste (NAU-K05B, Daiken Chemical Co., LTD) were used to prepare electrodes. Two samples with different electrodes were prepared. One was with the Au foil co-pressed onto one side of the pellet sample, and the Au paste coated onto the other side. The other one was with two electrodes of Au paste for comparison experiment. The Au paste electrode was

annealed at 450 K in vacuum for 10 hrs.

Temperature dependence of the d.c. current passing through the Au/C₆₀(OH)₂₄₋₂₆/Au structure was measured using a digital electrometer (ADVANTEST R8252) with a current resolution of 1 f A at various bias voltages from 10 to 200 V during heating up and cooling down processes. Schematic diagrams of two samples, the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste and the Au paste/C₆₀(OH)₂₄₋₂₆/Au paste structures were shown in Figs. 1 (a) and 1 (b). The sample was set in a vacuum chamber of a cryostat during the measurements. The base pressure of the vacuum chamber was less than 10⁻⁵ Pa. The d.c. current measurements were carried out in the course of heating up and cooling down processes between the temperatures from 50 to 450 K. The rate of heating or cooling was 0.14 Kmin⁻¹ with a stepwise increment of 1.0 K.

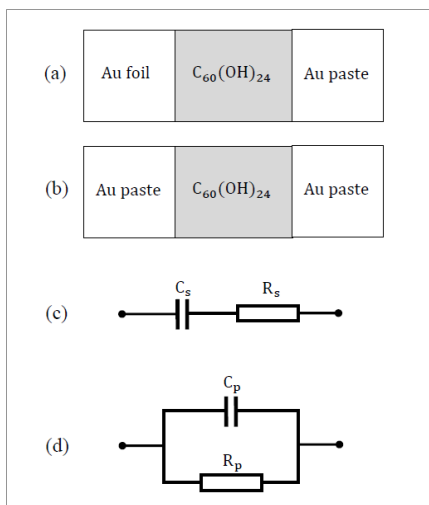


Fig. 1. Schematic diagrams of (a) the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste, (b) the Au paste/C₆₀(OH)₂₄₋₂₆/Au paste, and (c) the series and (d) the parallel equivalent circuit of the sample.

The a.c. impedance of the structure was measured at room temperature in atmosphere to separate the bulk and interface impedances by using Cole-Cole plot method. The impedance $Z = Z' + jZ''$ was used to characterize both resistance and capacitance by plotting the imaginary part $-Z'' = -\text{Im}[Z]$ versus the real part $Z' = \text{Re}[Z]$ of the a.c. impedance. The important information pertinent to the Au/C₆₀(OH)₂₄₋₂₆/Au structure can be obtained from the Cole-Cole plot. The dielectric properties of the Au/C₆₀(OH)₂₄₋₂₆/Au structure can be described by using the equivalent circuit shown in Figs. 1 (c) and 1 (d). The equivalent circuit of the series combination of resistance R_s and capacitance C_s in Fig. 1 (c) was used to draw the Cole-Cole plots. On the other hand, the parallel equivalent circuit in Fig.1 (d) was used to characterize bulk and interfacial resistance and capacitance, respectively.

3. Results and Discussion

Cole-Cole plots of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure, which were measured at a.c. amplitude of 0.1 V and at d.c. bias voltages, V_B , of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V are shown in Fig. 2 (a). The top and bottom panels were

plotted at linear and log scale on horizontal axis, so that, the plots at high frequencies can be seen in more detail in the bottom panel with log scale. It is clear in the figure that all Cole-Cole plots consist of two semicircles with different diameters. The diameters depend strongly on d.c. bias voltage. Because two semicircles correspond to bulk and interfacial resistance and capacitance of the structure, they change with d.c. bias voltage.

The Cole-Cole plots of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure, which were measured at a.c. amplitude of 3.0 V and at V_B of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V are shown in Fig. 2 (b) using both linear and log scales on horizontal axis. Two semicircles are observed in the figure and their diameters increase with increasing d.c. bias voltage. From the results in Figs. 2 (a) and 2 (b), we can conclude that the semicircles at left hand side, at higher frequencies, are correspond to bulk resistance and capacitance of the C₆₀(OH)₂₄₋₂₆ material. On the other hand, the semicircles at right hand side, at lower frequencies, are related to the interfacial resistance and capacitance of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure. The results indicate that there is a large polarization effect due to the OH groups in the sample because of large d.c. bias voltage dependence. The dielectric effect of C₆₀(OH)_n has been reported by several groups [6,12,13]. In order to analyze the dielectric properties of the Au/fullerenol interface in more detail, the parallel equivalent resistance and capacitance were also measured. The R_p and C_p of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 0.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0, and 2.5 V are shown in Fig. 3 as a function of frequency. They decrease with increasing a.c. frequency as well as increase with increasing d.c. bias voltage.

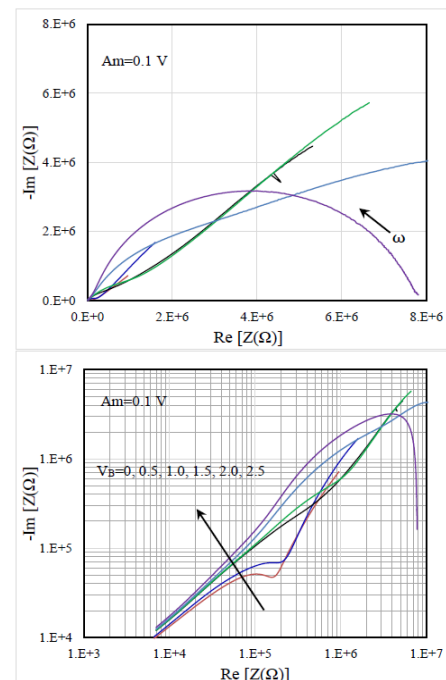


Fig. 2(a). Cole-Cole plots of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 0.1 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V.

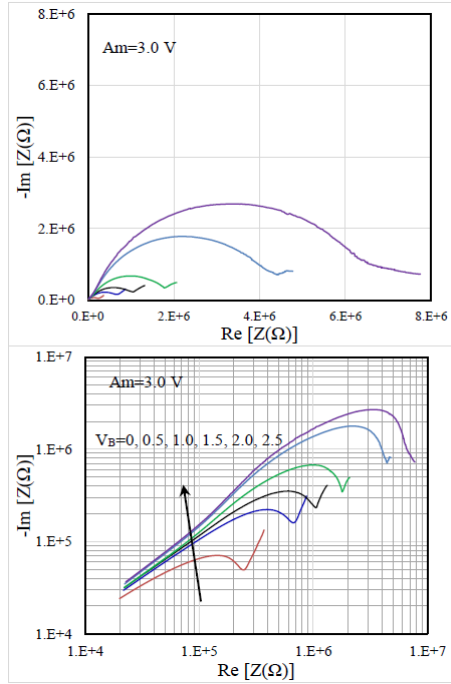


Fig. 2(b). Cole-Cole plots of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 3.0 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5 2.0 and 2.5 V.

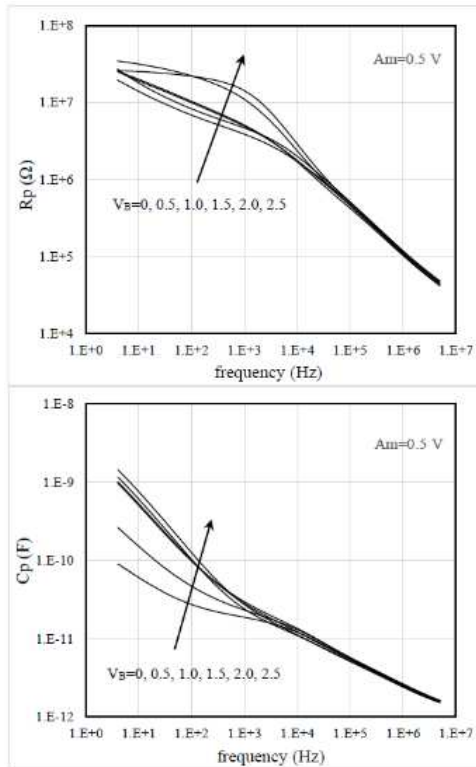


Fig. 3. The parallel equivalent resistance and capacitance of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 0.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5 2.0 and 2.5 V as a function of frequency.

The dielectric dissipation factor, $\tan \delta$, of the sample at a.c. amplitudes of 0.05, 0.5, 1.5, 2.5, 3.5 and 4.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5 2.0 and 2.5 V are shown in Fig. 4 as a function of frequency. It is clear in the figure that

the $\tan \delta$ decreases with increasing frequency. Also, there is a peak on $\tan \delta$ curve at frequency of 200 Hz at d.c. bias voltages below 1.5 V. The peak position shifts toward low frequency side when d.c. bias voltage is above 1.5 V. The result in the figure also shows that there is a peak on the $\tan \delta$ curves at frequencies below 10 Hz. It is well known that $\tan \delta$ is given by eq. (1):

$$\tan \delta = \frac{1}{\omega C_p R_p} \quad (1)$$

where ω is the angular frequency $= 2\pi f$ of the a.c. signal and $C_p R_p = \tau$, the time constant of the equivalent circuit of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure. When $\omega\tau = 1$, $\tan \delta$ has a maximum value and a relaxation phenomenon on dielectric response occurs.

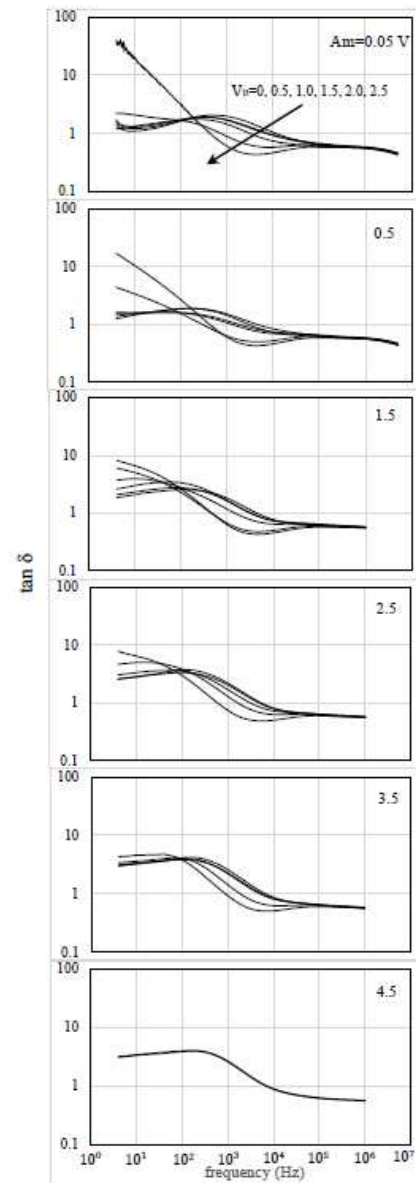


Fig. 4. The dielectric dissipation factor, $\tan \delta$, of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 0.05, 0.5, 1.5, 2.5, 3.5, and 4.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5 2.0 and 2.5 V as a function of frequency.

Cole-Cole plots of the Au paste/ C_{60} (OH) $_{24-26}$ /Au paste structure, which were measured at a.c. amplitude of 0.1 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V are shown in Fig. 5 (a). A semicircle with large diameter of about $10^6 \Omega$ can be seen in the top panel of the figure at low frequencies. It is related to the bulk equivalent resistance and capacitance of the C_{60} (OH) $_{24-26}$ material. The result is also consistent with that in Fig. 2. Also, two semicircles with smaller diameters are observed at higher frequencies in the bottom panel of the figure. As seen in the bottom panel, the second semicircle from the left side disappears at larger d.c. bias voltages. Therefore, we can conclude that the second semicircle from the left side corresponds to an interfacial phenomenon depending on the polarization of the C_{60} (OH) $_{24-26}$ material.

The Cole-Cole plots of the a.c. impedance of the Au paste/ C_{60} (OH) $_{24-26}$ /Au paste structure at amplitude of 3.0 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V are shown in Fig. 5 (b) at both linear and log scales on horizontal axis. The diameter of the semicircle, which is related to the C_{60} (OH) $_{24-26}$ bulk material, changes with increasing d.c. bias voltage. Also, the second semicircle from the left side disappears at higher d.c. bias voltages. These results are constant with that in Fig. 5 (a).

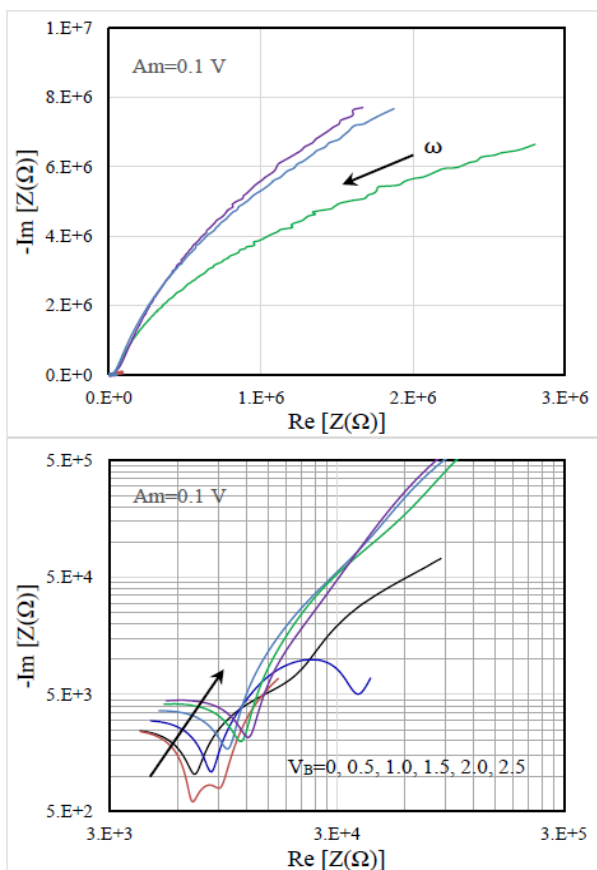


Fig. 5(a). Cole-Cole plots of the Au paste/ C_{60} (OH) $_{24-26}$ /Au paste structure at a.c. amplitude of 0.1 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V.

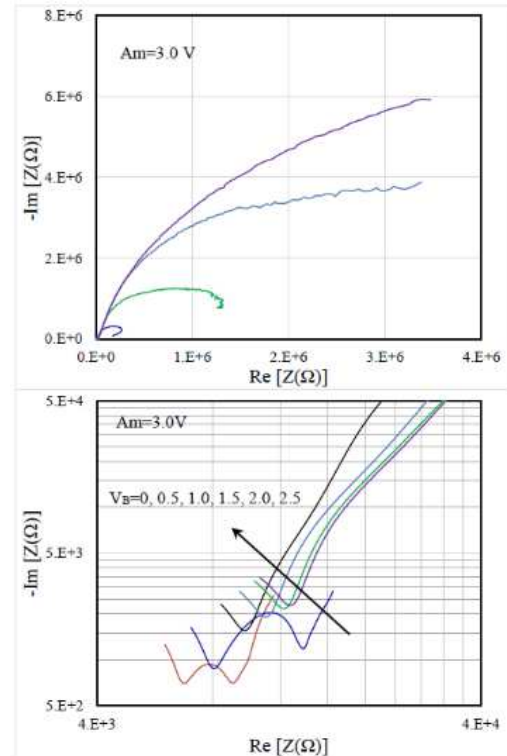


Fig. 5(b). Cole-Cole plots of the Au paste/ C_{60} (OH) $_{24-26}$ /Au paste structure at a.c. amplitude of 3.0 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V.

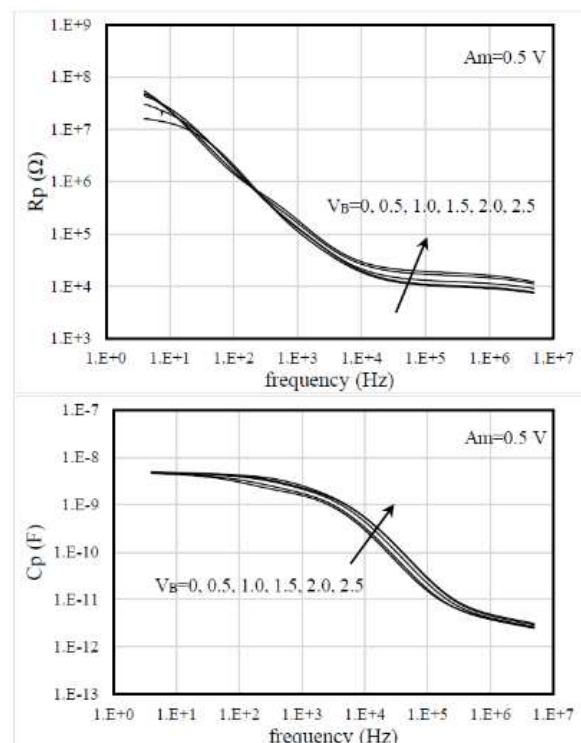


Fig. 6. The parallel equivalent capacitance and resistance of the Au paste/ C_{60} (OH) $_{24-26}$ /Au paste structure at a.c. amplitude of 0.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V as a function of frequency.

The parallel equivalent resistance and capacitance of the Au paste/ C_{60} (OH) $_{24-26}$ /Au paste structure at a.c. amplitude of

0.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5 2.0 and 2.5 V are shown in Fig. 6 as a function of frequency. The R_p and C_p decrease with increasing frequency. This is similar to the frequency dependence of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure as shown in Fig. 3. But, the R_p and C_p of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure in Fig. 3, depend more strongly on the d.c. bias voltages, in particular, at low-frequency side. This fact indicates that the semicircle with diameter of about $10^6 \Omega$ on the Cole-Cole plots in Figs. 2 (a) and 2 (b) is due to polarization of the C₆₀(OH)₂₄₋₂₆ material.

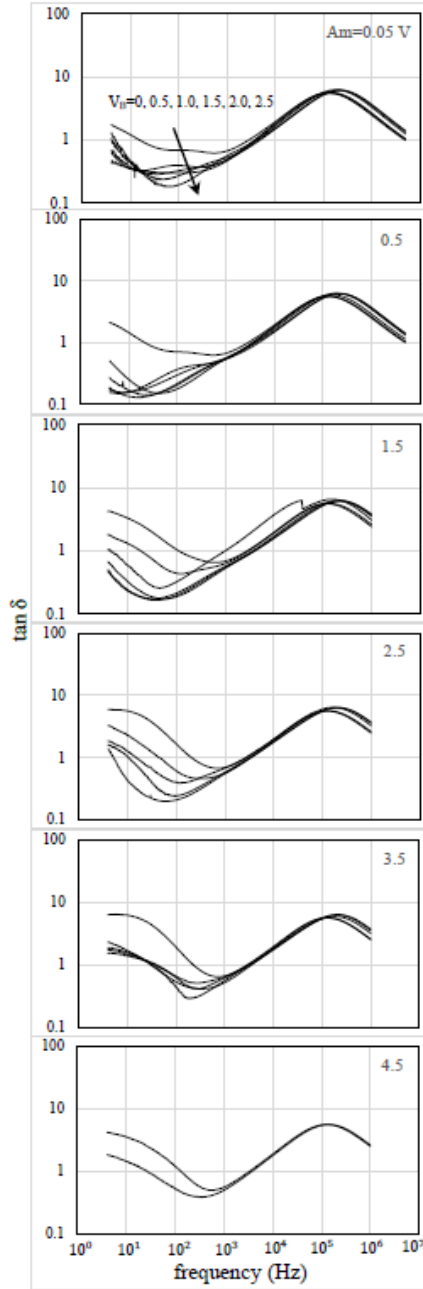


Fig. 7. The dielectric dissipation factor, $\tan \delta$, of the Au paste/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 0.05, 0.5, 1.5, 2.5, 3.5, and 4.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5 2.0 and 2.5 V as a function of frequency.

The dielectric dissipation factors of the Au paste/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 0.05, 0.5, 1.5, 2.5, 3.5, and 4.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5 2.0 and 2.5 V are shown in Fig. 7 as a function of frequency. There are two peaks on frequency dependences of the $\tan \delta$. The low-frequency peak below 10 Hz is similar to that of the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure, which is related to the Au electrode/bulk C₆₀(OH)₂₄₋₂₆ material contact. It depends on d.c. bias voltage due to polarization of the material. On the other hand, the high-frequency peak at 1.7×10^5 Hz cannot be observed in the Au foil/C₆₀(OH)₂₄₋₂₆/Au paste structure as well as the peak is almost independent to the d.c. bias voltage. By measuring frequency dependence of the $\tan \delta$ it is clear that there are two dielectric responses as $\tan \delta$ peaks due to interfacial resistance and capacitance for the Au foil/C₆₀(OH)₂₄₋₂₆ at 200 Hz and for the Au paste/C₆₀(OH)₂₄₋₂₆ at 1.7×10^5 Hz, based on a relationship of $\omega\tau = 1$ where ω and τ are from an applied a.c. signal and an internal relaxation process in the C₆₀(OH)₂₄₋₂₆ material.

The dielectric constants, ϵ_r , of the C₆₀(OH)₂₄₋₂₆ material, measured using the Au paste/C₆₀(OH)₂₄₋₂₆/Au paste structure at a.c. amplitude of 0.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V are shown in Fig. 8 as a function of frequency. The ϵ_r decreases with increasing frequency and no significant d.c. bias voltage dependence is observed. The ϵ_r value of the C₆₀(OH)₂₄₋₂₆ material is in the orders of magnitude of $10 \sim 10^4$. It is in good agreement with that of C₆₀(OH)₂₉ material, which was measured at room temperature by Ahmed *et. al* [6]. We also must point out that the ϵ_r of the C₆₀(OH)₂₄₋₂₆ material depends on temperature because of a rotation motion of the C₆₀ cage.

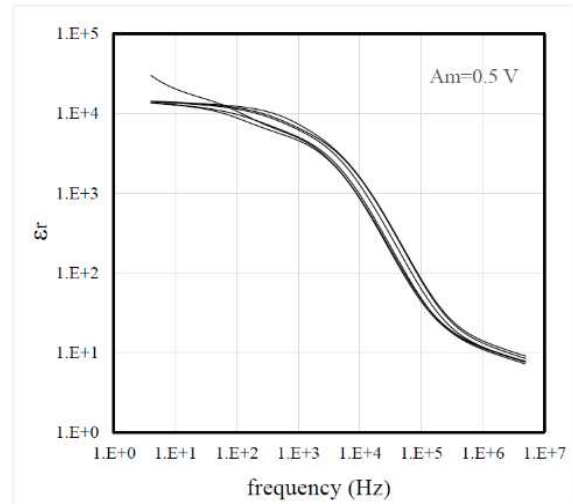


Fig. 8. The dielectric constant, ϵ_r , of C₆₀(OH)₂₄₋₂₆ material measured at a.c. amplitude of 0.5 V and at d.c. bias voltages of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 V as a function of frequency.

It was well known that dielectric constant of C₆₀ crystal is much small about 4.5 [14]. But, the ϵ_r of C₆₀(OH)₂₉ is in the range of $1 \sim 10^5$ in the temperature range of 220~320 K due to polarization of the OH groups on the surface of the C₆₀

cage [6]. Also, the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of fullerenols was reported to be dependent of the number of the OH groups [15-17]. Therefore, it is significant to measure electronic properties of the $C_{60}(OH)_{24-26}$ material with various number of the OH groups. The HOMO-LUMO gaps of $C_{60}(OH)_{10}$ and $C_{60}(OH)_{24-26}$, which were measured during heating up and cooling down processes are shown in Fig. 9 as a function of d.c. bias voltage. The gap of the $C_{60}(OH)_{10}$ is almost independent of existence of the OH groups, but a strong dielectric effect is observed on the HOMO-LUMO gap of the $C_{60}(OH)_{24-26}$ material. The gap increased more than doubled, from 500 to 1000 meV for changes of d.c. bias voltage from 10 to 180 V.

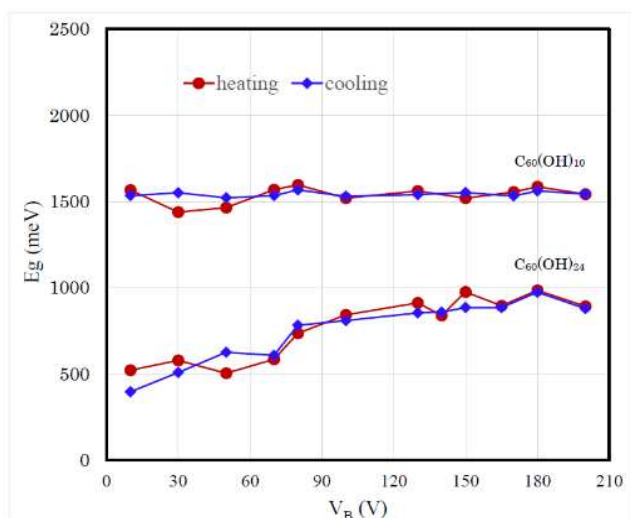


Fig. 9. The HOMO-LUMO gaps, E_g , of $C_{60}(OH)_{10}$ and $C_{60}(OH)_{24-26}$, measured during heating and cooling process as a function of d.c. bias voltage.

We are now in a position to discuss dielectric properties of the $Au/C_{60}(OH)_{24-26}/Au$ structure on the basis of the above results.

First, some physical properties such as equivalent resistance and capacitance, dielectric constant and HOMO-LUMO gap of the $C_{60}(OH)_{24-26}$ material change to easy with a.c. frequency, a.c. amplitude and d.c. bias voltage. These effects are related to polarization of the OH groups on the surface of the C_{60} cage and rotational motion of the $C_{60}(OH)_{24-26}$ molecules at room temperature. In fact, molecular rotation effects on dielectric property of the $C_{60}(OH)_{29}$ molecules have been reported [6].

Secondly, the $C_{60}(OH)_{24-26}$ material is an insulator and its resistivity has been obtained to be $3.9 \times 10^{13} \Omega\text{cm}$ from the d.c. measurement at room temperature in the present study. Three dielectric response characteristics of the $Au/C_{60}(OH)_{24-26}/Au$ structure are observed by analyzing Cole-Cole plots of a.c. impedance as well as dielectric dissipation factor. One is a dielectric response characteristic of the $Au/C_{60}(OH)_{24-26}/Au$ structure at frequencies below 10 Hz, regardless of preparation condition of the electrode, foil or paste. Other one the dielectric response characteristic of the Au/C_{60}

$(OH)_{24-26}$ material contact as a $\tan \delta$ peak at frequency of 200 Hz for the Au foil/ $C_{60}(OH)_{24-26}$. Finally, the dielectric response characteristic of the Au paste/ $C_{60}(OH)_{24-26}$ interface are observed as a $\tan \delta$ peak at frequency of 1.7×10^5 Hz.

Thirdly, it is possible to adjust dielectric response frequency of the $Au/C_{60}(OH)_{24-26}/Au$ structure by controlling preparation conditions of the Au electrode or by selecting metal materials. The Au foil electrode results in a dielectric response frequency of 200 Hz, but the Au paste electrode leads to a high frequency response characteristic at 1.7×10^5 Hz. These results are very important for electrode preparation of high-frequency or low-frequency electronic devices.

4. Conclusion

We have studied dielectric properties of the $Au/C_{60}(OH)_{24-26}/Au$ structure with different Au electrodes by measuring a.c. impedance and d.c. current in a wide temperature range. Three dielectric response characteristics were identified from Cole-Cole plots of impedance and dielectric dissipation factor. These dielectric response characteristics are very important for design and fabrication of electronic devices using fullereneol derivatives.

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