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Dielectric Properties of Self-assembled Monolayers of Dithiols

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Dielectric properties of dithiol self-assemble monolayers (SAMs) under ac electric field were presented. Using a Hg-SAM/SAM-Hg junction, the ac impedances of dithiol SAMs were measured using a sinusoidal perturbation of 30 mV (peak-to-peak) with the frequency ranging from 1 Hz to 1 MHz at zero bias. The contributions from dithiol SAMs and solvent interlayers were separated due to their different behaviors at ac impedance. The peak position in the loss spectra (the plot of tgδ *vs.* frequency) moves to low frequency with the increase of chain length of dithiols. Using a correlation of peak position with the chain length, the active energies of 23-39 meV for dithiol SAMs of C_6-C_{10} under an ac electric field were derived.

Key words: Dithiol self-assembled monolayers, AC impedance, Loss spectra

I. INTRODUCTION

With the shrinking of the semiconductor devices to the nanometer scale, there has appeared an urgent demand for a new generation of electronic devices both for technologic and economic reasons. Molecular devices have attracted a lot of study interest due to their promising physical and chemical properties, widely selective functional groups, identical molecular structure, and easy assembling on solid surfaces. Alkanethiol and alkanedithiol molecules, e.g. a long chain alkanethiol, have a low conductivity of $\sigma=(6\pm2)\times10^{-15}$ Ω^{-1}cm^{-1} with a dielectric constant $\varepsilon=2.7\pm0.3$ [1,2]. It has relatively high stability against the electrical breakdown. The electrical breakdown voltage was up to 3.2 V, and it can sustain a constant electric field up to $V=(8\pm1)\times10^{-8}$ V/m, thus it has been usually used as a ideal system in studies [1-9]. As a liquid metal, mercury has been a good substrate material for the growth of the self-assemble monolayers (SAMs) not only because of its atomically smooth, defect-free surface, but also because of its maximum contacting area as a soft electrode in the study of the molecules [10-13].

Using a metal-insulator-metal (MIM) junction, one can measure the electric conductivity, the electron transfer rate and the dielectric properties of the SAMs of different molecules with various chain lengths [1]. At present, the commonly used ways include using STM and dc cyclic voltammetry (CV) methods to measure the tunneling effect [9,12,13]. There have a lot of works studying the capacitance and the resistance of the SAMs [14], the covering rate to the mercury substrate [15], and the defect of the SAMs [16]. Recently, we have performed measurement of the frequency response of the alkanethiol in the ac electric fields [1].

In this work, we employed mercury and dithiols with different chain lengths ($HS(CH_2)_nSH$ (n=6,8,10)) to form the prototype Hg-SAM/SAM-Hg junction and measured the ac impedance spectrum. The relaxation mechanism for dithiol SAMs was also discussed.

II. EXPERIMENTS

Several alkanedithiols with various chain lengths, $HS(CH_2)_nSH$ (n=6,8,10), were purchased from Aldrich and used as received and used as received. Ethanol with spectranal grade was purchased from Riedel-de Haën. Ethanol solutions of dithiols (2 mmol/L) were prepared.

Figure 1 is a sketch map of the experimental configuration used in our measurement. A one-end-blinded glass tube of 2.9 mm in inner diameter with a sealed copper wire of 0.3 mm in diameter was put on an angle-adjustable slope. First, we transferred several drops of Hg into the tube and made the surface of an Hg drop close to the hole of a capillary which was connected to a microsyringe. The prepared dithiol solution was injected into the tube via the capillary with the microsyringe; then, we added another drop of Hg into the tube. The descending speed of the upper Hg drop was

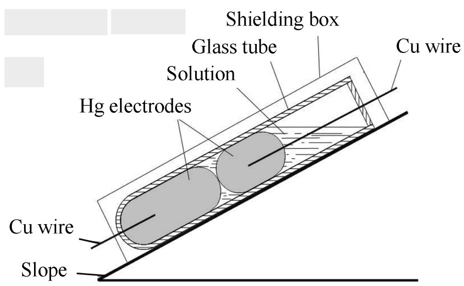

FIG. 1 Sketch map of experimental configuration.

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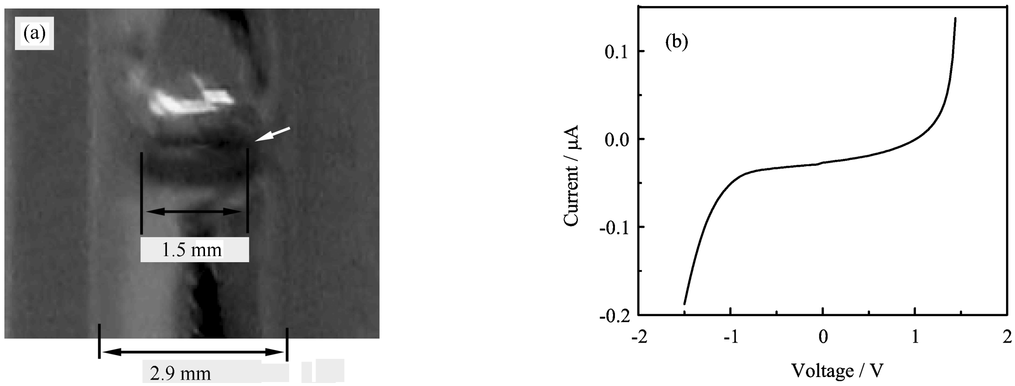

FIG. 2 (a) Microscope image of the contacted Hg electrodes, the contacted area is indicated by the white arrow. (b) A typical voltammetry behavior of the Hg-SAM/SAM-Hg junction.

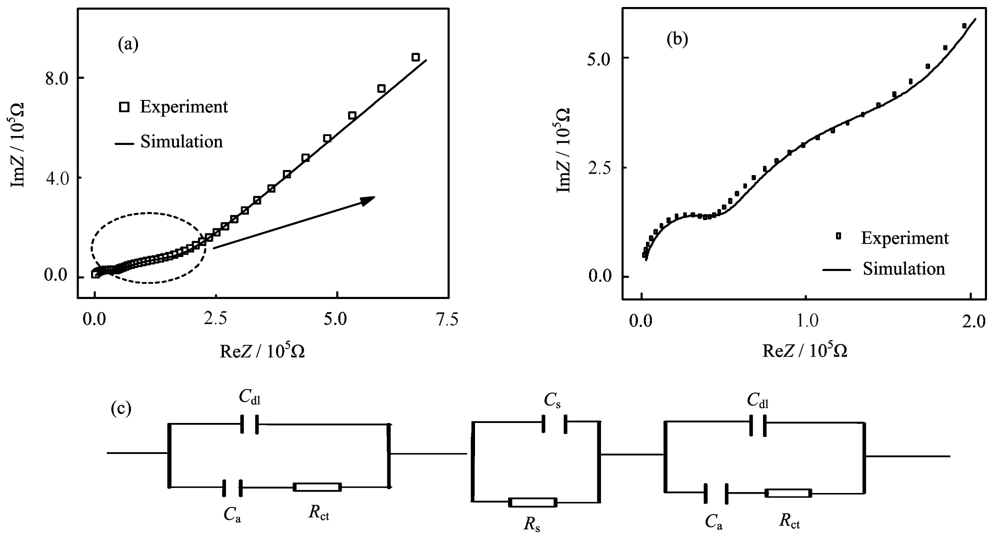

FIG. 3 (a) A representative Nyquist plot for C_8. Fitting parameters are $C_{\rm dl}$=25 nF, $C_{\rm a}$=90 nF, $R_{\rm ct}$=50 kΩ, $R_{\rm s}$=40 kΩ, $C_{\rm s}$=30 pf. (b) The amplification of the high frequency part of the Nyquist plot in (a). (c) The equivalent circuit representing Hg-SAM/SAM-Hg junction.

controlled by adjusting the angle of the slope. A copper wire of 0.3 mm was inserted into the upper Hg drop before it contacted with the lower Hg electrode. Typically, the junctions could sustain for about 5-10 h but became unstable after measurements of several cycles. The setup of the Hg-SAM/SAM-Hg junction was placed in an electric grounded shielding box. When the two Hg drop electrodes were brought into contact to form the Hg-SAM/SAM-Hg junction in an ethanol solution of a certain dithiol, we used a CHI 660A workstation to take the dc cyclic voltammetry. A Solatron SI 1260 was used to measure the ac impedance using a sinusoidal perturbation of 30 mV (peak-to-peak) with the frequency ranging from 1 Hz to 1 MHz at different biases.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the image of a typical Hg-SAM/SAM-Hg junction, the diameter of the contact areas of SAM-coated Hg drop electrodes was estimated to be about 1.5 mm. A typical voltammetry behavior of the Hg-SAM/SAM-Hg junction is shown in the Fig.2(b). A Nyquist plot for a junction of C_8 SAMs is plotted in Fig.3(a). Observed from this figure, the ac impedance spectrum is composed of two semicircles and one skew line. Like the Creager's model [6], our system can also be described by an equivalent circuit shown in the Fig.3(c). In the left-hand side and the right-hand side of the equivalent circuit, which describes the dithiol monolayers, a capacitor ($C_{\rm dl}$) representing the capacitance of the monolayers of dithiols is coupled in parallel to a resistor ($R_{\rm ct}$) representing the electron tunneling resistance coupled in series with a capacitor ($C_{\rm a}$) representing the adsorption pseudocapacitance (CPE). In the middle of the equivalent circuit, a capacitor ($C_{\rm s}$) representing the capacitance at the SAM/SAM interface is coupled with a resistor ($R_{\rm s}$) representing the resistance of the interface. In the model, a nearly symmet-

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rical structure is considered, that is, the two Hg-SAM electrodes are treated identically. Using this equivalent circuit, we can get the fitting curve of the Nyquist plot, which is shown as the solid line in the Fig.3(a). Both of these two curves have shown a good accordance.

The reciprocal of the fitted parameter $C_{\rm dl}$ was plotted against the chain length of dithiols in Fig.4. Using a relationship of

$$C_{\rm dl} = \varepsilon\varepsilon_0 S/d \tag{1}$$

where ε_0 is the permittivity of free space, $S\approx1.69$ mm^2 is the estimated contact area of SAM-coated Hg drop electrodes from the microphotograph, and d is the chain length of the dithiol, we got a dielectric constant $\varepsilon=2.6\pm0.2$, which is quite consistent with the values from the literature [1,2]. Hence, the model of the equivalent circuit is reasonable.

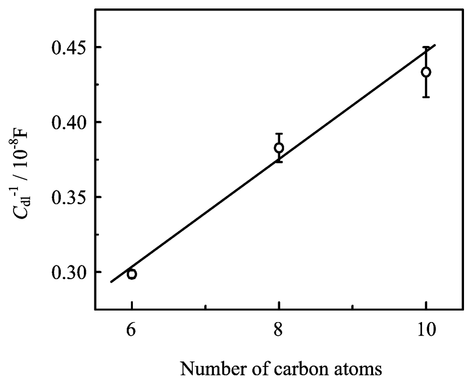

FIG. 4 Plot of the reciprocal of fit parameter $C_{\rm dl}$ against the chain length of dithiols.

Consider the relation

$$\varepsilon'(\omega) - j\varepsilon''(\omega) = d/j\omega\varepsilon_0 SZ(\omega) \tag{2}$$

we can get

$$\varepsilon'(\omega)C_0 - j\varepsilon''(\omega)C_0 = 1/j\omega Z(\omega) \tag{3}$$

where ε is the angular frequency, $j=(-1)^{1/2}$, $C_0=\varepsilon_0 S/d$ (C_0 is a constant for a given dithiol monolayers). From this relation we can get the relationship among the frequency, the imaginary and real parts of the dielectric constant, which is shown in the Fig.5 (a) and (b). Using the definition of the dissipation factor

$$\text{tg}\delta = \varepsilon''(\omega)/\varepsilon'(\omega) \tag{4}$$

where δ is the dielectric loss angle, we got the dissipation factor of the Hg-SAM/SAM-Hg junction with different chain lengths as a function of frequency, as plotted in Fig.6(a). At least two peaks are observed in each dissipation factor spectrum in the measured frequency range. Both peaks monotonically shift to low frequency with the increase of the carbon chain lengths.

For a clearer demonstration, we plotted the peak positions of dissipation factors as a function of chain length in Fig.6(b). Since the Hg-SAM/SAM-Hg junction is very complex, the ac impedance spectrum includes not only the information of the dithiol monolayer, but also the information of the interface of the SAM/SAM, therefore, it is difficult to distinguish the factors from each other directly. Thus, to deal with their different behaviors, a model of multirelaxation should be considered rather than a simple Debye model. Fortunately, the chain length dependence of the peak position of the dissipation factors provides us with some hints.

To understand the behaviors shown in Fig.6(b), we attempted to correlate the peak position at frequency to the chain length using a relation

$$\nu = \nu_0 \exp\left(-\frac{nE_{\rm a}}{kT}\right) \tag{5}$$

where ν is a frequency related to charge carriers, ν_0 is a constant, E_a is an active energy, k is the Boltzmann constant, and T is temperature. Using the relation, we fitted the peak positions of dissipation fac-

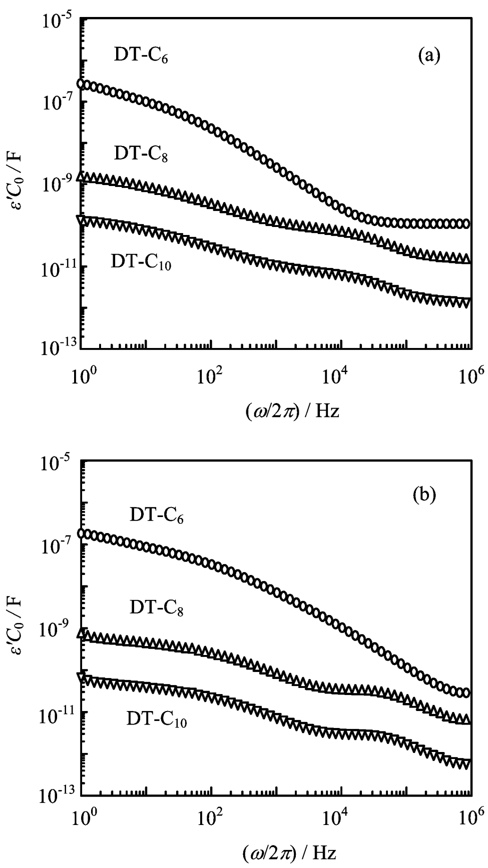

FIG. 5 Dielectric spectra of dithiols with different chain length: (a) Real impedance against frequency, (b) Imaginary impedance against frequency. The spectra are shifted by 10^1, 10^{-1} and 10^{-1} for clarity.

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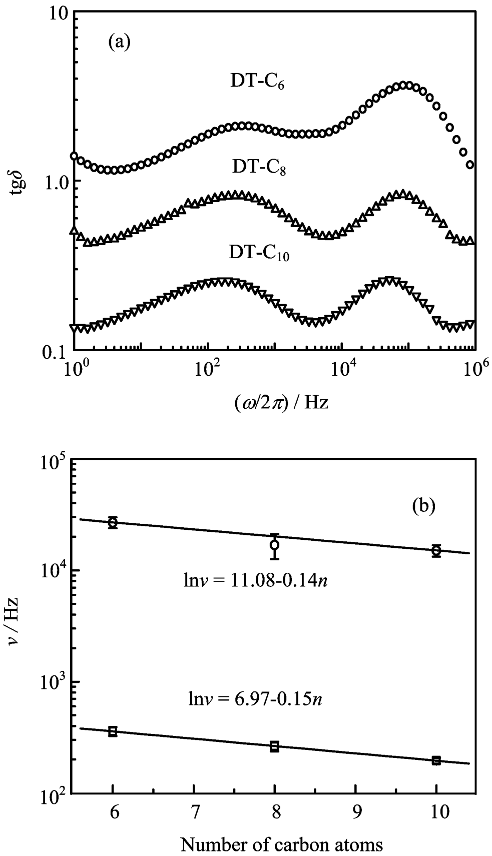

FIG. 6 (a) Dielectric loss spectra for dithiol SAMs with different chain length. The spectra are shifted for clarity. (b) Peak position against the chain length.

tors, as shown in Fig.6(b) and got the fit parameters of $\nu_0=8.9\times10^2$ Hz, E_a=3.9 meV for the peak at the middle frequency region and $\nu_0=6.5\times10^4$ Hz, E_a=3.7 meV for the peak at the higher frequency region. Both values of E_a are quite similar, which may reflect the behavior of molecular dipoles of the SAM. Then, we got the active energy ranging from 23 meV to 39 meV for dithiols of C6-C10 using the value for middle frequencies. The values describe the ability of response to the ac electric field for molecular dipoles, and are in good consistent with the value of the alkanethiols [1].

IV. CONCLUSION

In summary, using the Hg-SAM/SAM-Hg junction, we measured the dielectric properties of the dithiols. The different behaviors from the dithiol SAMs and the SAM/SAM interfaces are separated. The semicircles at higher frequencies in Nyquist plots are attributed to the effect of the SAM/SAM interfaces, and those at middle frequencies are attributed to the effect of dithiol SAMs. We have brought forward an equivalent circuit to describe the system, and the dielectric constant value obtained from the fit parameters is in good agreement with the values from the literature. This further indicates that our model used for fitting is reasonable. The dielectric loss spectra were analyzed. Two chain-length-dependent peaks were observed in the spectra of the dissipation factor (tgδ *vs.* frequency). Using a correlation of the peak position with the chain length we derived an active energies of 23-39 meV for dithiol SAMs of C_6-C_{10} under an ac electric field.

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