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Study on Charge Transport in Nanoscale Organic Monolayers for Molecular Electronics Using Liquid Phase Electrodes

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Abstract Incorporation of solid electrodes frequently involves plasma-based processing. The effect of plasma can influence the physical characteristics, depending on the magnitude in plasma. The undesired feature of plasma-induced damage should be prevented in characterizing the ultra-thin materials, such as ultra-thin films and organic monolayers. The current work at first proves the applicability of a liquid phase electrode in the electrical/dielectric properties through comparative work using Al and Hg on ultrathin Al_2O_3 films deposited through atomic layer deposition at low temperature: Two types of metals such as Aluminum (Al) and mercury (Hg) were used as electrodes in Al_2O_3 thin films in order to investigate the effect of electrode preparation on the current-voltage characteristics and impedance features as a function of thickness in Al_2O_3 film thickness. The success of Hg in Al_2O_3 thin films is applied to the AC and DC characterization of the organic monolayers obtained using the Langmuir-Blodgett method. From the DC current-voltage characteristics, the diode-like response is found to originate from the bulk response of the organic materials, evidenced by the fact and the capacitance is inversely related to the absolute thickness of organic layers.

Keywords: Molecular Electronics, Mercury, Electrical/dielectric, Langmuir-Blodgett Method, Current-Voltage characteristics

1. Introduction

Si-based microelectronics have been growing by enhancing the continuous scale-down in integrated circuits so as to accommodate the functionality and fuel market expansions in information-oriented products. The active development in CMOS (Complementay Metal Oxide Semiconductor) transistor devices has been based mainly on processing capabilities in combination with Si-based materials incorporating Si, SiO_x, and SiN_x. The continued growth will be likely to depend critically on the novel materials, processing, and/or device concepts, in order to replace the scale-down issue in Si-based semiconductors. In the scaling down of the conventional Si resolution below 0.1 micron, the SiO_2 dielectric should have a higher chance to experience unacceptable range of the leakage current, i.e. for the thickness less than 2 nm. The limitation can be overcome using atomic layer deposition of high permittivity materials, such as Al_2O_3, HfO_2, etc. The development trends are directed toward new dielectric materials and prompt innovation in processing equipment.

The strict ultra-thin materials are vulnerable to an external electrical shock, e.g., plasma damage which is frequently encountered through semiconductor device processing. The genuine physical properties of ultrathin oxide layers remain still to clarify. Semiconductor processing in thin film depositions are performed using plasma-assisited concepts, i.e., PECVD (plasma-enhanced chemical vapor deposition), PVD (physical vapor deposition), and dry etching. In order to remove the unintentional change

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in processing, a liquid phase electrode can be suggested as one of the solutions for characterizing the physical properties. As the first step toward the application of the liquid electrode to organic materials, the Al_2O_3 thin films are characterized using a solid and a liquid electrodes in the electrical/dielectric properties.

Molecular electronics have opened up a new research era, such as diodes, voltage-activated switches, and negative differential resistance elements[1-4]. The organic monolayer is much more fragile than the above-mentioned ultra-thin inorganic Al_2O_3 thin films. The phenomena of molecular electronics originate from the elementary molecular structure on the scale of 1 to 100 nm and the basic component can be formed through self-assembly, in combination with versatile aspects in materials synthesis, like rotaxane[4]. Space chare layers are proposed at the monolayer/metal interfaces which is employed to explain the hyeteresis behavior in the molecular device. The Langmuir-Blodgett (LB) method is believed to be a powerful fabrication method, allowing the formation of well-aligned molecular orientation at a molecular scale.

In this work, the effectiveness of a liquid electrode is proven in Al_2O_3 thin films through comparative study of aluminum and mercury electrodes as an initial step. Ultimately, the applicability of a liquid electrode to organic materials is demonstrated on organic monolayers obtained by the LB method, in terms of the DC and AC characterizations toward understanding charge transports in molecular electronics.

2. Experimental

Al_2O_3 thin films were fabricated using TMA (trimethylaluminum) and H_2O, using atomic layer deposition. The thickness ranges from 1.2 nm to 23.5 nm on the Si wafer, as determined through spectroscopic ellipsometry. The detailed processing conditions are summarized in Table 1. Extreme care has been made in order to control the quality of Al_2O_3 thin films, with emphasis on the cleaning step, before the aluminum oxide is deposited on the Si wafers through atomic layer deposition. Solid aluminum electrodes are formed on the Al_2O_3 specimens, using a metal shadow mask through dc sputtering. The diameters of the aluminum electrode are measured to be between 100 and 600 μm. In Hg, the amount of Hg is controlled through a microcyringe in order to obtain the mercury dot whose diameter is approximately, 200-400 μm. The diameters of Hg and Al are measured using the calibrated digital images obtained using a CCD camera. The typical image of a Hg drop on the Al_2O_3 thin films, is shown in Fig. 1 (a). The electroding configuration is constructed using a probe station with two micropositioners, as shown in Fig. 1(b). After the Al_2O_3 thin films are deposited on Si wafers, the specimens are attached on the glass substrate (Corning 1737) using Ag paste. After drying the paste, the Al_2O_3 specimens are characterized using micropositioners attached to the probe station, like a similar configu-

Table 1. Experimental processing conditions applied to atomic layer deposition of Al_2O_3 thin films

Contents	Condition	Contents	Condition
Working Pressure	3 torr	Substrate Temp.	200°C
Line Temp.	100°C	Source Exposure Time	0.5 sec
Source Temp.	90°C	Dep. Rate	1.1 Å/cyc

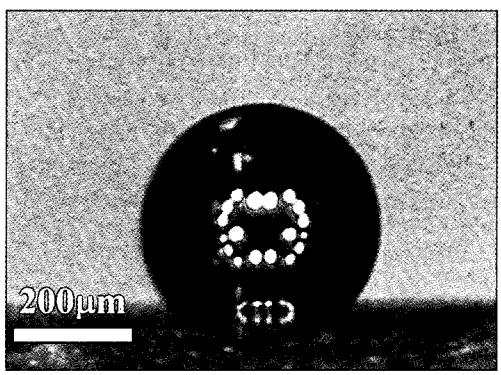


Fig. 1(a). A digital image on a mercury drop which is employed as an electrode in the MIM (Metal-Insulator-Metal) configuration.

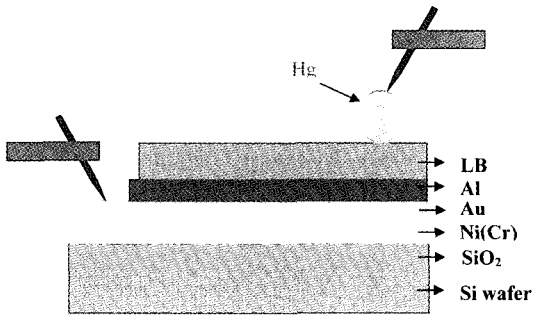


Fig. 1(b). Schematic Diagram of the experimental apparatus for measuring the electrical/dielectric characteristics in the Langmuir-Blodgett layers. (Al : 3000 Å, Au: 500 Å, and Ni(Cr): 300 Å).

ration as shown in Fig. 1(b), in order to compare the electrical and dielectric properties in terms of solid and liquid electrodes, e.g., Al and Hg.

Organic monolayers are prepared using a Langmuir-Blodgett method. In Langmuir Blodgett monolayers, *ASA*-15 ($C_{34}H_{46}N_2O_2$: molecular weight: 514.74) are used. The molecular structure is shown in Fig. 2. Langmuir isotherms of the ASA-15 were measured and then the Langmuir-Blodgett monolayers were deposited on substrates using an Langmuir equipment (Model 611D, NIMA, Coventrym UK) at ambient temperature. The area of one molecule (ASA-15) is 32Å^2 and the optimum film transfer pressure was determined using the π-A isotherms, approximately 25 mN/m which guarantees the 100% transfer ratio in the monolayer deposition. The subphase was chosen as a high-resistivity water (>18 Mohm·cm). Chloroform was used as a solvent about all kinds of amino style derivatives. The metal/monolayer/metal configurations are constructed like Fig. 1(b), The thin metallic layers on Si-wafer substrates are prepared using electron-beam evaporation. Initially, silicon oxides were grown on the top of Si substrates which was covered with an Ni-Cr alloy as an adhesive layer (300 Å) between the silicon oxide and gold. The gold electrodes are deposited using electron beam evaporation with the thickness of 500 Å. Al thin films (3000 Å) are deposited on the gold thin films, using electron beam evaporation. The final substrates were employed in forming Langmuir-Blodgett monolayers.

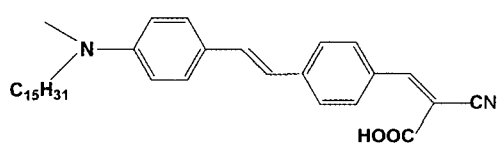
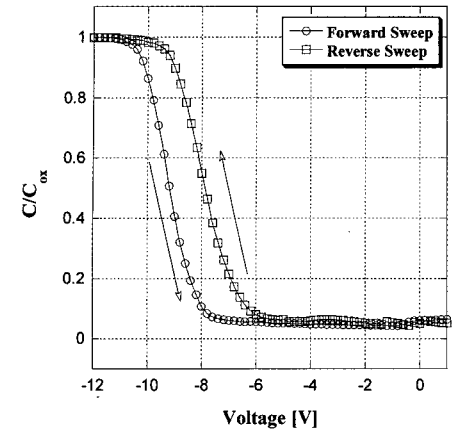


Fig. 2. Molecular structure of ASA-15 compound.

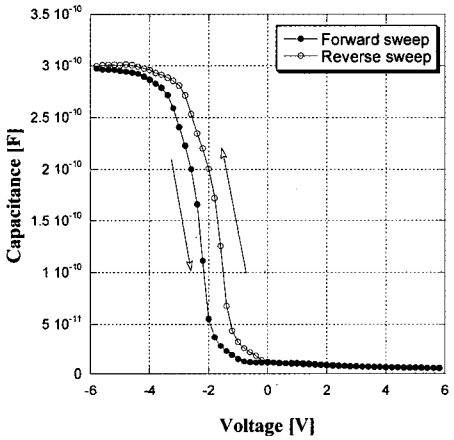
In order to investigate the effect of the thickness of monolayers, the dipping procedures are repeated up to 3 times without disrupting the underlying organic mono-layers. The direct current voltage-current behaviors are measured using a high-resolution electrometer (KE 6517A, Keithley Instruments, Inc., Cleveland, OH, USA) in a DC two point configuration. AC impedance spectra are obtained using a low-frequency impedance analyzer (HP4192A, Hewlett Packard, Palo Alto, CA, USA). The impedance spectra are collected from 1000 Hz to 1Mz in the logarithmic manners with the oscillating voltage of 1V.

3. Results and Discussion

Al_2O_3 thin films were chosen as a model system in order to investigate the effect of electrode materials on the electrical/dielectric properties, using solid and liquid electrodes, i.e., aluminum and mercury respectively, since the thickness can be controlled to atomic levels through the atomic layer deposition. The conventional electrical/dielectric characteristics of the metal-oxide-semiconductor (MOS) structure are characterized using Al or Hg as electrodes[5]. The capacitance-voltage characteristics are shown in Fig. 3 in Al and Hg, respectively. The overall behaviors are quite similar in accumulation, depletion, and inversion regimes. From the capacitance-voltage measurements, the critical parameters are obtained, i.e., dielectric constants from the accumulation and flatband voltage from depletion regime. The hysteresis in the C-V curve is caused by the type of trapping charges present in the oxide bulk, e.g., electron

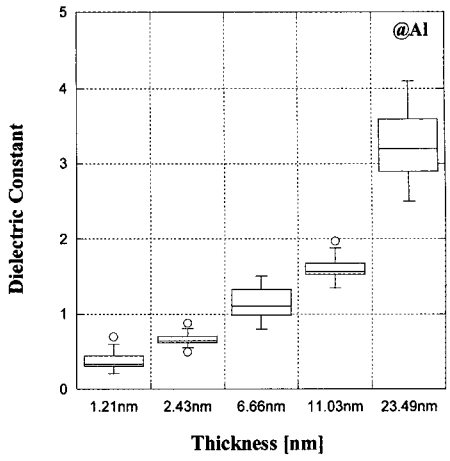


(a)

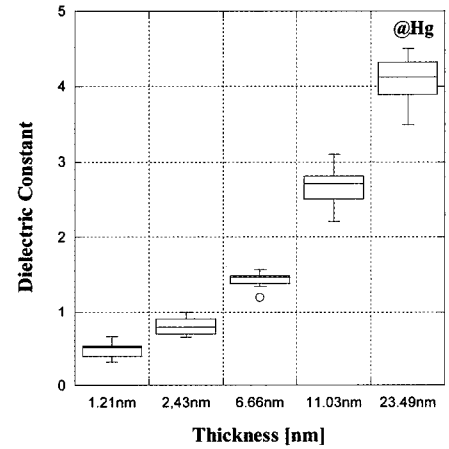


(b)

Fig. 3. Capacitance-voltage measurements using a) Al and b) Hg.



(a)



(b)

Fig. 4. Comparison of dielectric constants obtained using a) Al and b) Hg.

or hole trapping. As shown in Fig. 3., the reverse curve is less negative than the forward curve, indicating electron trapping in both Al and Hg. The information on the dielectric constants is compared using statistical box plots; leading to the reasonable agreement in the values.(See Fig. 4) Significant difference is not found in flatband voltages and flatband shifts as listed in Table 2. However, the current-voltage characteristics exhibited the dissimilar trends, in terms of breakdown voltage. Higher breakdown voltage is found in Hg electrodes applied as a gate metal as shown in Fig. 5. The beneficial effect is ascribed to the absence of plasma damage where highly energetic ion species are dominant in inducing physical damage in plasma-enhanced chemical vapor deposition, dry etching, and sputter-

Table 2. Variations of flatband voltages and the shifting in flatband voltages under a solid electrode (Al) and an liquid electrode (Hg)

Thickness (nm)	Flatband Voltage		Shift F.V	
	Hg	Al	Hg	Al
1.21	-1	-1.8	2	2
6.66	-1.8	-2.8	0.2	0.2
11.03	-3	-3.4	0.4	0.6
23.79	-4	-4.2	0.6	0.6

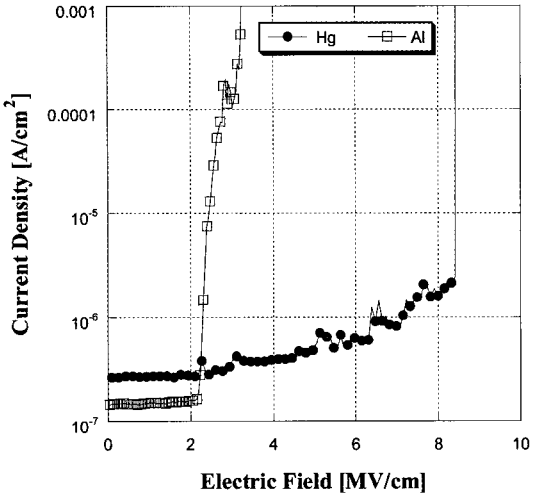


Fig. 5. Current-voltage characteristics in Al_2O_3 thin films using Al and Hg electrodes.

ing in semiconductor processing. The work functions of Al and Hg are 4.28 and 4.49 eV, respectively, showing that there is no significant difference in the physical feature.

As shown in the above experimental results on Al_2O_3 thin films, a liquid electrode is applicable to inorganic materials, irrespective of potential degradation due to plasma environment. Furthermore, the above statistical comparison (See Fig. 4) allows that the application of Hg to materials characterization is reproduced with high confidence levels, in both AC and DC modes. The organic monolayer is combined with the application of mercury, in the dielectric and electrical characterization. In particular, the direct current-voltage characteristics revealed the diode-like response along with the hysteresis in the I-V characteristics as shown in Fig. 6. In the positive voltage region, the significant hysteresis is found. The I-V characteristic can be understood, based on impedance spectra on the identical system, since the impedance spectra is strongly affected by whether the electrical/dielectric responses are due to the bulk and the interfacial features in electroceramics and polymers[6-8]. The impedance spectra are shown in Fig. 7(a). The corresponding dielectric information, i.e., capacitance is shown in Fig. 7(b). Fig. 7(b)

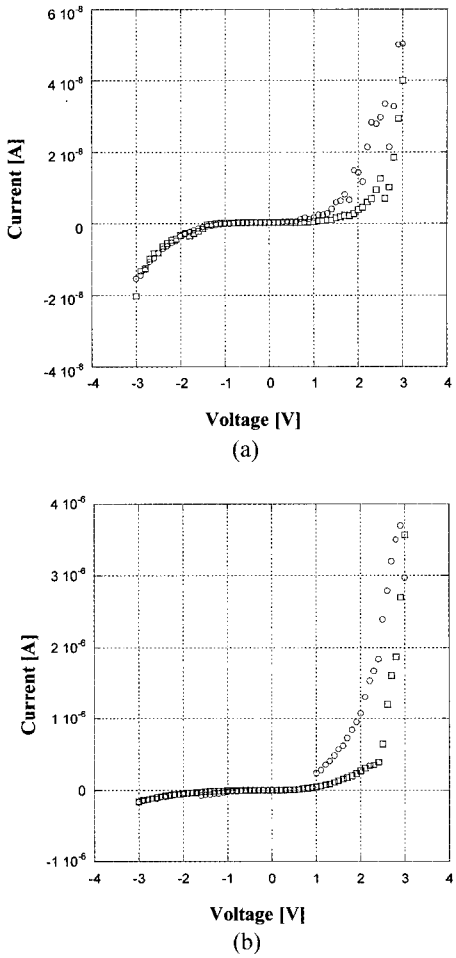


Fig. 6. Current-voltage characteristics as a function of the number of monolayers (a) 1 monolayer & (b) 3 monolayers.

shows that the inverse relationship between the capacitance and the thickness results from the inherent bulk response, not from the interface. The hysteresis of the MIM Metal-Insulator-Metal: Metal (Al)/ASA15/Metal(Hg)) originates from the asymmetric tunneling through an ordered monolayer. In the case structure of Pt/ASA-15 monolayer/Hg, most of the specimens have suffered from the problem of being shorted in the I-V characteristics, hindering one from measuring the current-voltage characteristic. The current Al/ASA monolayer/Hg behaves as a device like an diode. The aluminum oxide is believed to form on the aluminum electrodes, as a

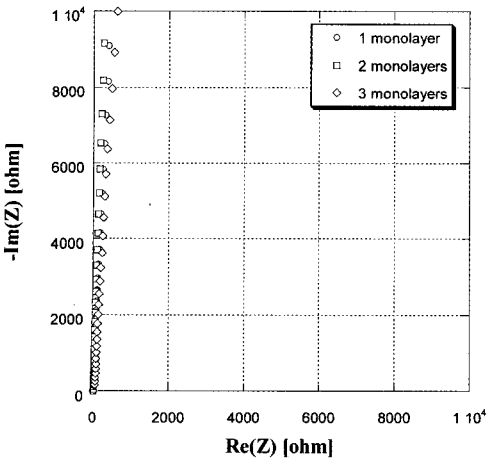


Fig. 7(a). Impedance spectra as a function of the number of monolayers.

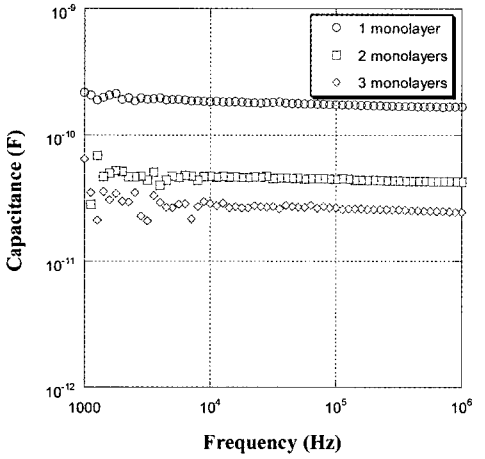


Fig. 7(b). Change in capacitance as a function of the number of monolayers.

natural oxide (less than 2 nm): whereas the application of a novel metal like Pt prevents the formation of the relevant oxides where robust layers of no defectives are difficult to fabricate; leading to the shorting between the top and bottom electrodes Therefore,. the function of an aluminum oxide is crucial to the requirement of hydrophilic surfaces in aiding the alignment of hydrophilic radicals in organic monolayers[8-14]. The resultant organic monolayers are more robust and less defective, allowing the reasonable capacitance with hundreds of mm patterns. The presence of the native oxide is believed to enhance the formation of the organic monolayers.

Electrical/dielectric characteristics in nanoscale thin layers can be made through the combination of direct current and alternating current modes, i.e., DC current-voltage characteristics and AC impedance spectroscopy, leading to highly reproducible and reliable measurements. Conventionally, solid electrodes such as Al, are applied to the thin films through various plasma-based deposition in order to investigate the charge transport and evaluate the physical properties in thin films. The noble metals, Pt, Au, and Ag, cannot allow the oxide on the corresponding surface, with the danger of being reacted between Hg and noble metals spontaneously. The second issue is plasma damage which is related to the formation of pinholes and short circuits, The above-mentioned issues causes the experimental problems which require high degree of reproducibility and reliability in nanoscale materials. The current approach suggests the liquid electrode of Hg as a nondestructive probing tool in molecular electronics. Furthermore, the applicability of Hg is largely influenced by the defect-free mono-layers formed on the bottom electrodes. The mechanism of hysteric behavior in current-voltage characteristics is nor fully understood. This work demonstrates that the current-voltage characteristic is a generic property of organic materials, assisted by the presence of aluminum oxide, in combination with a nondestructive electrode of Hg.

4. Conclusions

In summary, we have demonstrated a nondestructive electrical/dielectric probing method in a two terminal metal/molecular-monolayer/metal planar device structure, involving mercury as one of the electrodes in nanoscale inorganic Al_2O_3 thin films and organic mono-layers, excluding the artifacts and structural damage which may be induced through electrode preparation. As a first step, the Hg and Al electrodes were attempted simultaneously in thin Al_2O_3 films deposited through atomic layer deposition in terms

of the electrical/dielectric information, i.e., breakdown voltage, dielectric constants, and flat band voltages: the combined characterization leads to the result that Hg can replace Al as a electrode in measuring the electrical/dielectric properties. The approach of using Hg eliminated the lengthy and defective preparation which can affect the physical properties. The nature of liquid electrodes exhibited the inherent characteristics in breakdown voltage and leakage currents. Ultimately, impedance measurement on organic mono-layers indicates that the simple MIM device behaves as a capacitor exhibiting the hysteresis in the current-voltage responses. Liquid electrodes are shown to be an easy and reproducible tool for monitoring the nanoscale materials which is sensitive to the external parameters.

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