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Investigation of Unconventional Semiconducting Material

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Abstract:

In recent years the semiconducting industry has been seeking alternative semiconductor to the traditional silicon-based materials. Prototypes of field effect transistors using conjugated organic polymers as semiconductors (1) have been developed for its low manufacturing cost and the ability to be flexible (2) as well as forming arrays of large areas (3). In our experiments we have shown that a potentially new category of unconventional semiconducting material may have been found. The semiconducting layer consists of a monolayer of copper II ions complex on the surface of a self-assembled monolayer of 16-mercaptohexadecanoic acid (MHA) used as gate dielectric. In our experiment, we constructed an organic thin film transistor using polyimide as the substrate, self-assembly monolayer of 16-mercaptohexadecanoic acid (MHA) as gate dielectric, and copper electrodes as gate, source, and drain. Removal of copper ions from the MHA surface using EDTA (ethylenediaminetetraacetic acid) has been shown to have the effect of decreasing semiconductivity, while addition of copper ions to the surface can increase semiconductivity. A compound with similar chemical composition to the MHA-Cu$^{2+}$ interface but with different structure, copper II formate, has also been tested for semiconductivity. With copper II formate showing no apparent semiconductivity, we have concluded that the semiconductivity of the MHA-Cu$^{2+}$ interface originates from its structure. Thus our unconventional semiconductor can be described as transition metal ions complexing on the surface of fixed and orderly packed carboxylic acid groups.

Introduction:

Prior to this summer a PhD student from University of Illinois at Chicago, Dong-Un Jin, was experimenting with the construction of an organic thin film transistor device. Jin used self assembly monolayer of MHA as the dielectric layer and deposited copper electrodes using electroless plating techniques (4). Fig. 1 shows a schematic representation of the device he constructed without the semiconducting layer.

![Fig. 1. Schematic diagram of Jin’s transistor device without the semiconducting layer.](image)
With the device, gate modulation was observed. This was a surprise since no known semiconducting material has been applied.

![Graph showing gate modulation observed in the absence of silicon semiconducting material.](image)

**Fig. 2.** Gate modulation observed in the absence of silicon semiconducting material.

As shown in figure 2, as the gate voltage increased to the negative direction, the amount of current flowing between source and drain electrodes increased correspondingly. The plots of current flow show gate modulation, which was the characteristic of a semiconductor. One should also notice that on figure 2, the amount of current flow decreased as the gate voltage became positive, indicating that the semiconducting mechanism was only valid under negative gate voltage. With these clues we set out to investigate the potentially new category of semiconductor.

By reviewing the protocol of the synthesis of the organic thin film transistor, we discovered that in order to carry out the electroless deposition of copper, the device must be submerged under copper sulfate solution (4). This allowed unreduced copper II ions to form complex with the carboxylic acid groups on the surface of MHA gate dielectric. The complexation of copper II ions to the MHA surface has been studied and published by other researchers (5). In our experiments, we investigated two possibilities that might contribute to the semiconductivity, the chemical composition and the structure of the MHA-Cu$^{2+}$ interface.

Copper II formate, a transition metal salt of copper II ion and carboxylic acid, resembled the MHA-Cu$^{2+}$ interface in terms of chemical composition. However, their structures were very different. Tetra-hydrated copper II formate had a shape of octahedral, carrying two carboxylic acid groups and four ligand water molecules. The MHA-Cu$^{2+}$ interface, on the other hand, had an orderly packed carboxylic acid surface. In order to determine if the chemical composition of copper II ions complexing with the carboxylic acid groups were the origin of semiconductivity, we constructed bottom-gate design field effect transistors using highly-doped silica as the gate electrode, silicon
dioxide as gate dielectrics, and copper as source and drain electrodes. Gate modulation was tested after copper II formate were applied to the channel between source and drain electrodes with its solutions with concentrations of 0.4, 0.04, and 0.004M. With our transistor devices, we observed no apparent semiconductivity of copper II formate. Our results were confirmed using another field effect transistor obtained from Motorola, which also indicated no semiconductivity to copper II formate.

A different set of experiment were designed to test if the structure of the interface contributed to the semiconductivity. Replications of organic thin film transistors that Jin used to observe gate modulations were made. Coppers were electrolessly plated on polyimide substrates to make electrodes, while the MHA gate dielectrics were made to self-assemble in ethanol solution under 60 degrees C. Gate modulations were observed on these devices. Afterwards, copper ions from the interface were removed using EDTA (ethylenediaminetetraacetic acid). We observed a decrease in gate modulation after the treatment with EDTA. Finally, the device was submerged under copper II formate solution in order to restore the copper ions to the interface. The results showed an increase in gate modulation. With these results, we concluded that the structure of fixed carboxylic acid surfaces of MHA with copper II ions could be characterized as an unconventional semiconductor. Its performance and actual mechanism of semiconductivity were yet to be determined.

**Methods:**

We chose highly doped silicon as the gate electrode material because the dielectric layer can be constructed simply by oxidizing the surface of the wafer into silicon dioxide, SiO₂. In order to control the thickness of the oxidized layer, the oxidation rate of silicon wafer had to be measured. The silicon wafer was first etched using 3:1 hydrogen peroxide and sulfuric acid for thirty minutes and hydrofluoric acid for one minute in order to remove native dioxide layer. The etched wafer was then placed into *Lindberg Blue/M 3-Zone Furnace* for oxidation. Four runs of experiments were performed with furnace temperature set at 600, 700, 800, and 1000°C. The thickness of the growing oxidized layer was monitored after 1, 3, 5, 10, 15, 20, 30, and 60 minutes of oxidation. The thickness of the oxidized layer was observed using an ellipsometer. The ellipsometer emitted a beam of polarized light onto the sample surface. A fraction of the beam would be reflected off the surface of the oxidized layer, while the rest would be reflected off the wafer surface. The phase difference between the two reflected beams allowed the software to compute the oxidized layer thickness in Å. A schematic representation of an ellipsometer is illustrated below:

![Fig. 3. Schematic view of an ellipsometer (6).](image)
The presence of SiO$_2$ was confirmed using *Fourier Transformation Infrared Spectrometer* (FTIR). The FTIR used beam splitter to separate the infrared light from the source into two paths. The two beams were reflected from mirrors, one stationary and one mobile. By moving the mobile mirror, the interfering pattern over a range of wavelength could be observed. By comparing with the background spectrum recorded before the oxidation, the interfering pattern could be converted to absorbance spectrum through the algorism of *Fourier Transformation*. The signature peak around 1260 cm$^{-1}$ revealed the presence of SiO$_2$. A schematic diagram of FTIR is illustrated below:

![Schematic diagram of FTIR](image)

A working curve of SiO$_2$ thickness as a function of oxidation time was constructed using data obtained. With the working curve, three samples of highly doped silicon wafer were prepared with SiO$_2$ layer thickness of 200, 500, and 1000 Å. Copper was chosen for the source and drain electrode material for its conductivity and low cost. The oxidized wafers were placed in the sputtering chamber. Sputtering Deposition Method was used to deposit copper electrodes on the wafer. The copper source was bombarded with electron, knocking off copper atoms. The copper atoms would deposit onto the wafer surface.

With the electrodes made, we were ready to deposit copper (II) formate onto the transistor. 97% hydrated copper (II) formate was used. Aqueous solution of copper (II) formate with concentration of 0.4M, 0.04M, and 0.004M were prepared. These concentrations were chosen because we were trying to recreate the experimental condition when Jin observed the gate modulation, and 0.04M of Cu$^{2+}$ was the concentration of the electroless deposition solution he used (4). The solutions were applied between the source and drain electrodes and left to dry for 48 hours. Gate modulation was then tested.

To further assess our theory, another experiment was designed. We made a duplicate of the device which Jin observed the gate modulation. The specification of the device was as below:

![Device specification](image)
The device was constructed by depositing copper metal on the polyimide substrate using commercially available copper electroless plating solution (4). After the copper was plated, the device was submerged in the 10mM MHA solution in ethanol with 60°C hot water bath for one hour. This allowed the self-assembly monolayer of MHA to grow on the copper surface (8). Finally, the copper electrodes were patterned onto the top of the device with the same electroless plating solution used previously.

After the device was constructed, gate modulation was tested. If gate modulation was to be observed in the absence of known semiconducting material, the device would be rinsed with 0.008M EDTA solution (ethylenediaminetetraacetic acid) for 5 minutes. According to our theory, the gate modulation of this device was tied to the presence of residual transition metal ions on the surface of MHA. EDTA would remove the transition metal ions from the surface and therefore reduce the degree of gate modulation (9).

After the organic thin film transistor was treated with EDTA and tested for gate modulation, the device was submerged under 0.4M copper II formate solution as an attempt to restore copper ions in the conducting channel. According to our theory, replenishing copper ions to the device should restore or even increase the degree of gate modulation. This theory was put to test at this step. Copper II formate solution was used because of its similar chemical composition to the MHA-Cu<sup>2+</sup> interface, which would reduce the risk of introducing interfering ions. Furthermore, copper II formate would eventually be proven to have no apparent semiconductivity. Use of copper II formate solution would insure us that the increase of gate modulation was not due to other uncontrolled materials in the solution.

**Results:**

Growth curves of SiO<sub>2</sub> on the highly-doped silicon wafer:

![Fig. 5. Schematic diagram of an organic thin film transistor used to observe the effect of EDTA chelation.](image)
From the oxide growth curve we can see that the oxidation rate increased with temperature and decreased with oxidation time. This result fits our expectation since higher temperature allowed more kinetic energy for the reaction to occur. As oxidation time prolongs, oxygen molecules must diffuse through thicker SiO₂ layer in order to oxidize more silicon. Thus the reaction rate slowed down as the time progresses.

FTIR Measurements of oxidized silicon wafer:

FTIR data at 1000°C:
Growing peaks around 1260 cm$^{-1}$ show the presence of SiO$_2$. The noise of these spectrums came mainly from internal reflection. Since we were using one-side polished wafer, we could not observe percent transmittance as commonly used in FTIR experiment since the light could not go through the sample. Instead we observe the light reflected off the surface of the wafer. Internal reflection thus
creates fluctuation on the baseline. The noisy peaks around 1400 cm\(^{-1}\) and 3800 cm\(^{-1}\) came from O-H bonds in water molecules. Since we had to use aqueous solution to etch the wafer, water molecules would be present on the surface of the wafer. In addition, water molecules in the air would also be detected by the sensitive equipment.

Results of Gate Modulation Test on 200Å Dielectric Thickness Device:

![Current as The Function of Source-Drain Voltage, Gate Voltage Sweeping from Positive to Negative](image)

Fig. 9. Current measurement on the sample transistor with 200Å dielectric layer. The voltage between drain and source was swept from +10V to -10V. The gate voltage was swept from +3V to -3V.
Current as A Function of Source-Drain Voltage, Gate Voltage Sweeping From Negative to Positive

Consistent results were obtained when the gate voltage was swept from both positive to negative and from negative to positive.

The plot appears similar to gate modulation behavior. However, closer examination of the data reveals the difference. A typical plot for gate modulation behavior of a semiconductor should report minimum current flow when no gate voltage is applied, while the current flow increases as gate voltage increases. Our results, sweeping the gate voltage from +3V to -3V, shows intermediate current flow when the gate voltage is zero, minimum current flow +3V gate voltage, and maximum current flow at -3V gate voltage.

The result suggested no gate modulation behavior of the material tested. However, we soon discovered that this result was not reliable, as the leakage current of the transistor was too high for the device to express the property of copper II formate. We adjusted the apparatus to measure the current flowing from the gate to the drain electrode. For an ideal transistor this current should be minimal, around the order of $10^{-11}$ A (10). Our data revealed currents between gate and drain electrodes were in the range of $10^{-3}$ A.
It was unexpected for the SiO₂ dielectric to fail. SiO₂ has minimum effective dielectric thickness around 7Å (11), while we had over 200Å of SiO₂ on our device. Our original theory focused on the
possibility that copper atoms might have disrupted the integrity of the dielectric layer during the deposition to the extend that allowed electrons to tunnel into the conduction band of the dielectric material. However, the results from the device with 1000Å dielectric layer made this theory questionable.

**Leakage Current of 1000Å Dielectric Thickness Device:**

![Leak Current With 1000Å Dielectric Layer](image)

Fig.13. Current measurement between gate and drain electrodes. The voltage difference between source and drain electrodes were kept constant. Gate voltage was swept from 0 to 6V. The leakage current was 10 times smaller than what was observed on the device with 200Å dielectric. However, this was still too high for the transistor to be functional.

At 1000Å thickness, we did not expect copper atoms to have enough kinetic energy to penetrate SiO$_2$ layer. This suggested that there must be another reason for the dielectric layer to fail. In addition, the test for gate modulation on this device also showed no apparent semiconductivity for copper II formate. However, since the device had high leakage current, we could not reach a solid conclusion with this result.
Some literatures suggest that dopant from the silicon wafer may diffuse into the dielectric layer and reduce its performance (12) (13). Since we were using highly doped silicon (doped with boron) and oxidizing at high temperature (1000°C), such possibility is high. Our attempt to reduce boron diffusion into the SiO₂ layer was to oxidize the wafer at lower temperature. Since SiO₂ growth rate is lower at low temperature, we used a combination of wet and dry oxidation method in order to obtain enough dielectric thickness within reasonable amount of time.

Until this point we had been using only dry oxidation, which was achieved simply by oxidizing the wafer in an oxygen environment at a controlled temperature. The reaction for dry oxidation is:

\[2\text{Si} + \text{O}_2 \rightarrow 2\text{SiO}_2\] (4)

When using wet oxidation, the wafer is oxidized under saturated water vapor. Oxygen gas was first pass through distilled water to produce saturated vapor, then it was fed into the furnace where the oxidation occurred. The chemical reaction of wet oxidation is:

![Graph showing transistor test at dielectric layer 1000Å]
Si + 2H₂O → SiO₂ + 2H₂ (15)

This reaction is faster than the dry oxidation reaction and thus produces better yield (15). The drawback for wet oxidation was that the dielectric layer formed is less uniform in thickness and may have surface defects (15). A transistor with 170Å SiO₂ thickness was prepared by wet oxidation with oxygen as carrier gas under 700°C for two hours and under 750°C for one additional hour. The setup of the device was shown below:

Fig. 15. By using oxygen as carrier gas, we employed a combination of dry and wet oxidation under 700 degrees C. This gave us the faster reaction rate of wet oxidation and the reliability of dry oxidation.

The transistor was immediately put to test for its leakage current. Its leakage current was 10³ to 10⁴ times smaller than that of the transistors prepared using dry oxidation.
Unfortunately, with the newly constructed device, we did not see the result we expected. The result showed no apparent semiconductivity for copper II formate. The current measured between source and drain electrodes did not increase as the magnitude of the gate voltage increased.

Fig. 16. Leakage current of the transistor device constructed using low temperature oxidation. The leakage current is 3 to 4 orders of magnitude smaller than the leakage current observed from the devices fabricated at 1000°C.
In order to confirm our result, we obtained a functional transistor device from Motorola and tested copper II formate with it. The result again showed no gate modulation pattern.
With the result obtained, we have concluded that copper II formate does not have semiconductivity.

We have failed to recreate the condition when Dong-Un Jin first observed gate modulation using copper II formate. Further experiments were designed in order to investigate alternative possibilities for the cause of gate modulation that Jin observed.

In order to investigate if copper ions ever played a role in the gate modulation observed on Jin’s organic thin film transistor at all, we constructed the same device with identical specification. The presence of carboxylic acid groups on the surface of the MHA dielectric layer was confirmed using FTIR.
Again with no apparent semiconducting material we tested the gate modulation of the device. The result showed gate modulation behavior similar to Jin observed previously.

Fig. 19. FTIR spectrum of the constructed organic thin film transistor. The two peaks around 2900 cm\(^{-1}\) represent the methyl groups from MHA molecules. Peaks at 1700 represent the carboxylic acid groups on the surface of the dielectric.

Fig. 20. The transistor device showed gate modulation in the absence of known semiconducting material.
After five minute rinsing using EDTA, the effect of gate modulation decreased as predicted:

As shown above, after rinsing with EDTA, the change of gate voltage had little effect on the current flowing between source and drain electrodes. Therefore the lines representing different gate voltage overlapped with each other. In other words, gate modulation had been reduced or removed from this device using EDTA rising. This was a good evidence to support our theory that copper ions played a role on the semiconducting property observed on the organic thin film transistor device. Furthermore, the amount of current between the source and drain electrodes also decreased from $10^{-3}$ to $10^{-4}$. This could be interpreted as another support of our theory about the copper ion. If the copper ions played a role in carrying charges with semiconducting property, we expect the amount of charges to be carried through to decrease as the amount of copper ions available decreased.

Finally, the device was submerged under 0.4M copper II formate solution for 15 minutes as an attempt to replenish copper ions in the channel. The result is shown below:

![Graph showing the effect of gate modulation after EDTA rinsing and copper II formate treatment.](image-url)
Our result showed the ability to increase and decrease gate modulation via addition and removal of copper ions from the device. This is a strong evidence to support our theory of the interfacial structure of the device and its semiconducting property.

**Conclusion:**

Although some organic transition metal salts have been shown to have semiconductivity (12), copper II formate does not show apparent semiconductivity according to our experimental results. We have tested copper II formate using bottom-gate transistors fabricated in our lab as well as one acquired from Motorola. Neither result showed any gate modulation.

With our other experimental results, we have concluded that the interfacial structure on the surface of MHA dielectric layer has semiconducting property. The interface can be described as well-oriented and fixed carboxylic acid with copper II ions complexing on top of the carboxylic acid structure. Two possible structures were proposed and shown below, while the exact one is yet to be determined. The left figure shows protonated carboxylic acid groups, while the copper II ions are stabilized by coordinating interactions with lone pair electrons from the oxygen. The right figure shows deprotonated carboxylic acid groups, while the ions are stabilized by ionic interaction.
The experimental results have shown that the extent of gate modulation can be decreased or removed via removal of copper ions using EDTA chelation. On the other hand, the effect of gate modulation can be restored or increased by replenishing copper ions to the surface. These are strong evidences that led us to believe that copper II ions played an essential role in the semiconductivity of the device. When Dong-Un Jin saw the gate modulation effect on his device, there must have been residual copper II ions from the electroless plating solution (1) of the source and drain electrodes on the surface of MHA that enabled the device to express semiconductivity.

While the source of semiconductivity has been identified, its mechanism requires more investigation. My theory regarding to the semiconducting mechanism focused on the delocalized nature of the electrons on the interface. As positively charged ions, copper II formate ions have diffused valence electrons because the positively charge nucleus repels the positively charged electron shells. The carboxylic acid groups on the other hand have delocalized negative charges between two oxygen atoms as shown below:

With diffused electrons on the copper ions and the delocalized charges on the MHA surface, the
electrons may diffuse across the entire interface, forming a charge carrying channel.

As shown above, charges may move across the interface along the diffused electrons when voltage is applied between the source and drain electrodes. When negative voltage is applied to the gate electrode, the negatively charge gate electrode pushes more electron density from the carboxylic acid groups into the diffused electron band and increase its charge-carrying ability. This would also explain why the device shows decrease in gate modulation under positive gate voltage. When the gate electrode is positively charged, it pulls electron density of the carboxylic acid groups away from the interface, which decrease the delocalization of the electrons.

As our experiments have set an initial step, much more future works are required in order to complete the investigation of this type of semiconducting mechanism. The charge carrying mobility needs to be characterized for this type of material. The charge carrying mobility is proportional to the response time, that is, the performance of the device. Therefore the charge carrying mobility must be characterized before the practical use of such device can be determined. Furthermore, experiments on how to improve the interfacial structure that would yield better performance should be conducted. Different transition metals and organic functional groups can be used to observe the difference in performance. The optimum range of copper ion density also needs to be determined. Most importantly, the actual mechanism of the semiconducting property of this material will be solved in future experiments.

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