CHEMISTRY LETTERS, pp. 863-866, 1986.

CHEMICALLY PREPARED POLY(N-METHYLPYRROLE) THIN FILM. ITS APPLICATION TO THE FIELD-EFFECT TRANSISTOR

Akira TSUMURA, Hiroshi KOEZUKA, Sei TSUNODA, and Torahiko ANDO
Materials and Electronic Devices Laboratory,
Mitsubishi Electric Corporation,
1-1, Tsukaguchi Honmachi 8-Chome, Amagasaki, Hyogo 661

A thin film of poly(N-methylpyrrole) has been prepared by a chemical method. The chemical structure of the polymer resembles that of the electrochemically prepared one. A fild-effect transistor has been fabricated utilizing the polymer as a semiconducting material.

Conducting polymers consisting of a π-conjugated backbone are very attractive because of their unique electric and electronic properties. For examples, some kinds of the conducting polymers have been demonstrated to be used as very light electric wires instead of heavy metal ones, and/or they are also candidates of electrode materials for light-weight rechargeable batteries. Many studies have been performed in order to increase their electric conductivity and to synthesize new stable polymers for various applications.

The authors have believed that conducting polymers can also be utilized in electronic devices as active components. One of the authors (H.K.) has previously reported that the electrochemically prepared conducting polymers with the conductivities in semiconducting region have promising properties as semiconductors: the p-doped copolymer film having pyrrole and N-methylpyrrole unit has been demonstrated to make an excellent Schottky type junction with an indium metal.[1,2] It has also been reported by Wrighton and his coworkers that some kinds of electronic devices having diode-like or transistor-like characteristics can be fabricated by using electrochemically prepared conducting polymers.[3] The devices operate according to electrochemical redox reactions, and the conducting polymers act merely as electrical conductors.

In this study, we will demonstrate a field-effect transistor with a conducting polymer, which can operate in the solid state. Fig.1 shows the schematic cross-sectional view of the fabricated FET device.

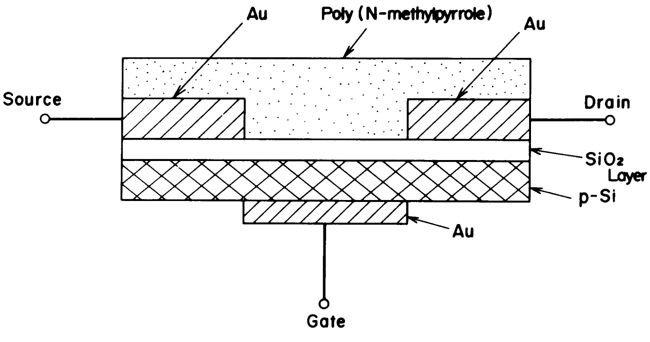

Fig. 1. Schematic cross-sectional view of the fabricated FET device.

The fabrication process is described as follows. A p-type silicon wafer (B-doped, 0.05-0.1 S/cm, <100>-axis, 300 μm thick) was thermally oxidized in O_2 gas to be covered with SiO_2 layer of ca. 300 nm thick. The SiO_2 layer on one-side of the wafer was stripped by plasma-etching. Gold was vacuum evaporated on the naked surface in order to obtain an ohmic contact to the wafer. The two Au electrodes (*i.e.*, Au-coated Cr-electrodes ; Au=100 nm, Cr=200 nm thick) separated from each other by 10 μm (gap width = 2 mm) were prepared on the SiO_2 layer of the other side by vacuum evaporation and photolithographic technique.

N-methylpyrrole was purchased from Tokyo Kasei Ltd. and was distilled under a reduced pressure and was preserved under a nitogen atmosphere until use. The poly(N-methylpyrrole) (PNPy) film was prepared by a chemical polymerization method.[4)] N-methylpyrrole of 1 ml was added into the reaction vessel containing 100 ml-aqueous $FeCl_3 \cdot 6H_2O$ (0.1 mol/dm^3) solution kept at 25-27 °C. The polymerization of N-methylpyrrole was immediately initiated by the oxidant (*i.e.*, Fe^{3+} of $FeCl_3$) dissolved in the solution. A sample substrate placed in this solution in advance was coated with a very thin polymer film after 2 hours. The PNPy so formed was ca. 300 nm thick. The polymer film completely covered the two Au electrodes and the SiO_2 layer between them. The obtained sample was washed with water and ethanol, blown with pure N_2 gas and dried *in vacuo*.

The obtained thin film was identified by FT-IR spectra to be poly(N-methylpyrrole), and it has a little more carbonyl groups than electrochemically prepared one. The existence of Cl^- ions and neutral Fe atoms in the film was also detected by means of X-ray photoelectron spectroscopy (XPS). These are thought to be the residues of the oxidative reagent. The visible spectrum of PNPy shows a broad absorption band and the band gap was roughly estimated to be ca. 2.43 eV from the spectrum, which is close to the value (2.4 eV) of electrochemically prepared one.

All of the electrical measurements were carried out *in vacuo* using a Yokogawa-Hewlett-Packard 4140B pA meter/dc voltage source and a Yokogawa-Hewlett-Packard 4192A impedance analyzer. The electrical conductivity of the film was measured using a Au/PNPy/Au sandwitch type cell, which yielded straight I-V characteristics. The obtained value was much smaller (ca. 2×10^{-5} S/cm) than that (ca. 1×10^{-3} S/cm) of the electrochemically prepared PNPy.[7)] This is probably due to the shorter conjugation length for the chemically prepared PNPy compared with the case of the electrochemically grown one, considering that the PNPy in this study has more carbonyl groups. Although Cl^- ions is detected by means of XPS, it is thought that they do not effectively act as dopants. The Schottky type diode was fabricated in order to confirm that the PNPy prepared in this study is a p-type semiconductor. As well known, the low work function metals such as indium and aluminum make the Schottky type junctions with p-type semiconductors. The PNPy was sandwiched with a gold and an indium electrode. When negative voltages were applied to the indium electrode, the low impedance states were observed. The Mott-Schottky plot gave a straight line. These results indicate that the Schottky type junction is formed at the interface between the PNPy and the indium metal, and that the PNPy is a p-type semiconductor.

In the fabricated FET device (Fig.1), the Au electrode is used as a source and/or a drain electrode. The p-Si wafer itself and the SiO_2 layer act as a gate electrode and a gate insulator, respectively. The typical I-V characteristics of the device are shown in Fig.2. The voltage axis represents the drain voltage (V_{DS}) relative to the source electrode connected to the earth, and the current axis is the source current (I_S) which equals to the drain current (I_D). When the gate voltage is zero volt (V_G =0 V), the current passed between drain and source electrodes (I_S) linealy increases with V_{DS}. However, as V_G becomes more negative, I_S rises more steeply and has a tendency to saturate. This phenomenon occurs reversibly. It is suggested that this phenomenon is attributed to the so-called "field effect " which is usually observed in conventional inorganic semiconductor devices.

The operating mechanism for the device is qualitatively illustrated with Fig.3. Holes are majority carriers of electricity in the p-type PNPy. They are uniformly dispersed in the thin film under the zero gate voltage (Fig.3(a)), which leads to the high resistance between the source and the drain. They will be attracted to the interface between two Au electrodes (Fig.3(b)) when

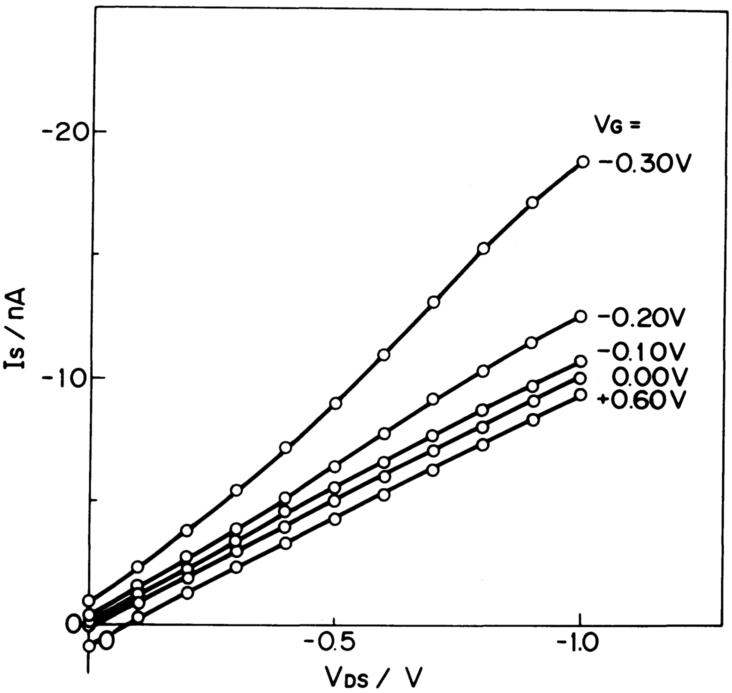

Fig. 2. Source current (I_S) vs. drain voltage (V_{DS}) characteristics of the fabricated FET device at various gate voltages (V_G).

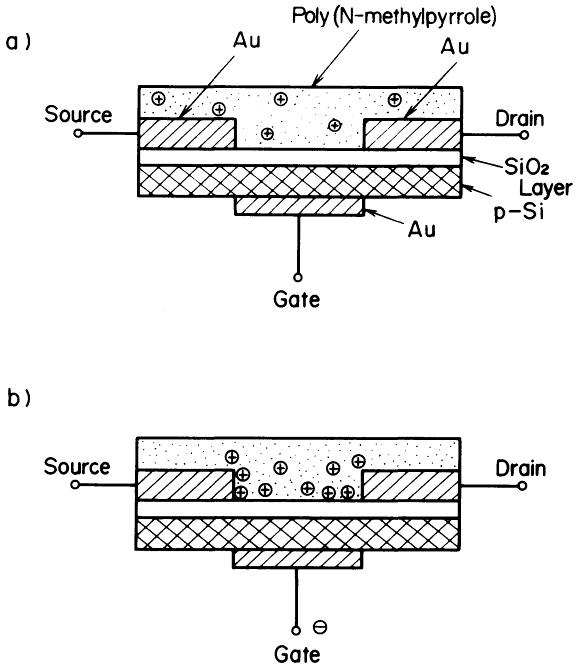

Fig. 3. Operating mechanism for the fabricated FET device. a) Gate voltage is zero volt. b) Gate voltages are negative.

negative biases are applied to the gate. Under such circumstances, the resistance between the two Au electrodes is considered to decrease by applying negative biases to the gate. It is, therefore, elucidated that the field-effect is caused by the accumulation of holes at the interface between the PNPy thin film and the gate insulator. The field-effect mobility μ_{FE} of holes is roughly estimated to be ca. 1×10^{-2}-1 cm^2/Vs from the I_S-V_G curves at constant V_{DS}.6)

In conclusion, we have fabricated a FET device where a chemically prepared PNPy film is utilized as a semiconducting material. The observed field-effect is considered to be caused by the accumulation of holes between the interface of the PNPy thin film and the gate insulator. The formation of the inversion layer by minority carriers is not observed. The roughly estimated field-effect mobility μ_{FE} of holes is ca. 1×10^{-2}-1 cm^2/Vs.

We are now studying the relationship between the semiconducting characteristics of conducting polymers and their chemical structures in order to construct the FET devices with excellent properties.

References

1) H.Koezuka and S.Etoh, J.Appl.Phys., 54, 2511 (1983).
2) T.Ogama and H.Koezuka, J.Appl.Phys., 56, 1036 (1984).
3) H.S.White, G.P.Kittlesen, and M.S.Wrighton, J.Am.Chem.Soc., 106, 5375, 7389 (1984).
4) M.Aizawa, H.Shinohara, and H.Shirakawa, Polymer Preprints, Japan, 33, 495 (1984).
5) K.K.Kanazawa, A.F.Diaz, R.H.Geiss, W.D.Gill, J.F.Kwak, J.A.Logan, J.F.Rabolt, and G.B.Street, J.Chem.Soc., Chem.Commun., 1979, 854.
6) S.M.Sze, "Physics of Semiconductor Devices," Wiley, New York (1981).

(Received February 21, 1986)