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# Partial Carbonization of aromatic polyimide films

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Aromatic polyimide (UPILEX S) films are carbonized at 1000℃. Electrical conductivity of the carbonized films is found to be $\sigma = \sigma_0 \exp(-E/kT)$, $\sigma_0 = 0.001$ A $V^{1}$ $m^{-1}$, $E = 0.02$ eV. The Hall coefficient was found to be negative, i.e. carriers are electrons. Carbnized polyimide films are n type semiconductors. If it is an n type semiconductor, the impurity level was found to be 0.314 eV below the conduction band. The carriers density $\eta_e$, was found to be expressed as $\eta_e = 1.18 \times 10^{13} \exp(-0.0067 \text{ eV} / kT)$ $m^{-3}$ and carrier mobility $\eta_e = 0.19 \exp(-E/kT)$ $m^2$ $V^1$ $S^{-1}$.

Key words: Aromatic polyimide, carbonization, n type semiconductor, carrier density, carrier mobility

## 1. INTRODUCTION

Aromatic polyimides have excellent properties such as heat-resistance, electrical insulation and chemical resistance. Kapton supplied by du Pont Co. or UPILEX by Ube Industries, Ltd. are examples of commercially available aromatic polyimide films.

No condensation water is evolved during thermal treatment. It has a glass transition temperature near 285℃. The film can be used at high temperature 400~450 ℃. A distinct melting point is not found but softening point and glass transition point is expected above 360 ℃. Carbonized films can be bent and not brittle as glassy carbon films. It may be quite useful to study electronic properties of partially carbonized aromatic polyimide films. Partially carbonized films are amorphous carbon still coutaining nitrogen, hydrogen etc. Hydrogen will be remained until 1300 ℃ and nitrogen is remained until 1700 ℃. It is known that graphite is a semi−metal, but the electronic properties of amorphous carbon are not well known. Usual amorphous carbon available contains a lot of impurities. Carbonized films can be bent and not brittle as glassy carbon films. It is quite useful to study electronic properties of partially carbonized aromatic polyimide films. Partially carbonized films are amorphous carbon still containing nitrogen, hydrogen etc. Hydrogen will be remained below 1300 ℃ and nitrogen below 1700 ℃.

## 2. METHODS

UPILEX S type (trade name of Ube Industries, Ltd) films of thickness 75μm and 20μm, were cut to $4.5 \times 10^{-2}$ m length, $2.4 \times 10^{-2}$ m width. The film was sandwiched between graphite blocks and fixed by a wire. The assembly was put in a quartz tube and hydrogen gas was flown. After a few minutes, a voltage of 100V was applied. The temperature was measured by an alumel-chromel thermocouple with a digital-multimater. After the temperature reached to 1000 °C, hydrogen gas was continuously flown until the temperature was cooled to 200 °C. Aluminium foil copper electrodes were attached to the carbonized polyimide film with silver paste, The aluminium foils

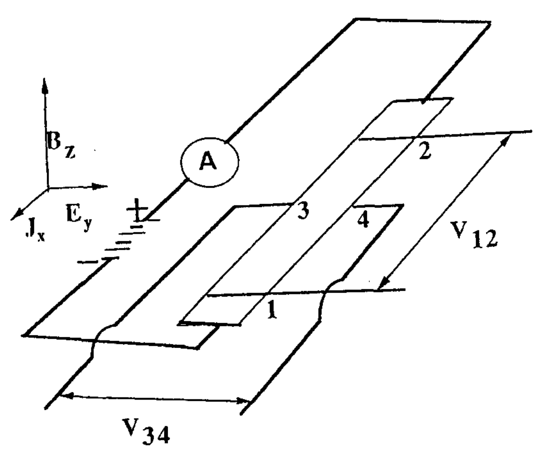


Fig. 1. Schematic diagram of experimental arrangement

were connetected to copper foils using silver paste and the film was sandwiched between acrylic boards. A chromel-alumel thermo couple was attached near the specimen foil. The assembly was sandwiched by Nb-Fe-B magnets whose magnetic field was about 0.5T at the specimens The whole assembly was put in a plastic bag and immersed into silicone oil heated by a controlled heater. The electrical resistance was measured by four point method. The current through the film, between the terminals 1 and 2, the Hall voltage $V_{34}$, the gauss meter voltage to measure the magnetic field and the thermocouple voltage were measured by five digital voltmeters. The data were acquired every 0.25 ℃ by a personal computer. A schematic diagram of the circuit is shown Fig. 1.

3. RESULTS AND DISCUSSIONS

The polyimide films were carbonized between 700 ℃ and 1000 ℃. It was found that the electrical conductivity can be expressed as

$$\sigma = \sigma_o \exp(-E/kT) \quad (1)$$

where k is the Boltzman constant. T is the absolute temperature. $\sigma_o$ and E are found to be $4\times10^{-5}$ s $m^{-1}$ and 0.4 eV respectively. The electrical conductivity is higher as the carbonization temperature is higher. It was found that the electrical conductivity of the film carbonized in hydrogen atmosphere was higher than that carbonized in nitrogen atmosphere. It is likely that the dangling bonds became in active by hydrogen is caught by dangling bonds and the mean free path of carriers is longer in the film carbonized in hydrogen atmosphere than those carbonized in nitrogen atmosphere.

The Hall coefficient R is given by

$$R = E_y / (B_z J_x)$$

where $E_y$ , $B_z$ and $J_x$ are electric field in the y direction, magnetic field in the z direction and electric current density in the x direction, respectively. x, y, and z are rectangular coordinates.

The experimental data show that R is negative, this implies that the carriers are negatively charged, i.e. electrons. The electrical conductivity was found to be larger at higher temperature (eq(1)). These results suggest that the specimens are n type semiconductors or semi−metals. The carrier density $\eta_e$ is given by

$$\eta_e = (|e|R)^{-1}$$

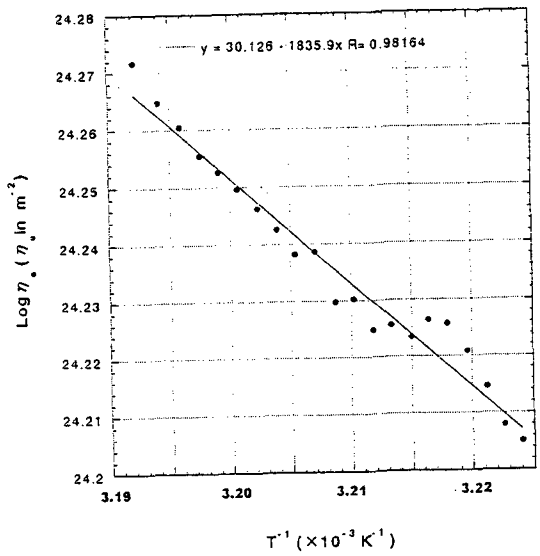


Fig. 2. Logarithum of carrier density vs. inverse of measuring temperature.

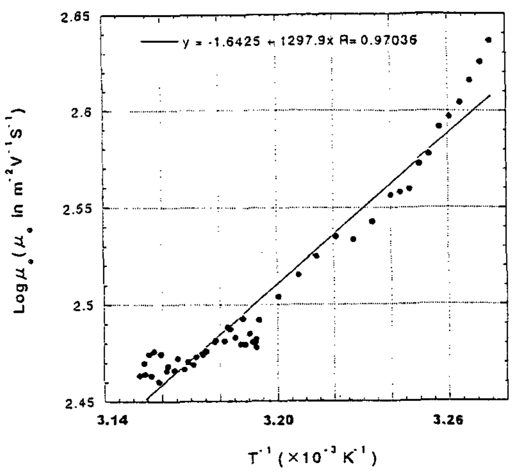


Fig. 3. Logarithum of carrier mobility vs. inverse of measuring temperature.

and the mobility $\mu_e$ is

$$\mu_e = \sigma / (\eta_e |e|),$$

where |e| is the absolute value of the electron charge and $\sigma$ is the electrical conductivity.

*ln* $\eta_e$ and *ln* $\mu_e$ are plotted in Figs. 1 and 2, respectively.

Fitting

$$\eta_e = A_1 \exp(-E_1 / kT)$$

and

$$\mu_e = A_2 \exp(E_2 / kT)$$

one finds $A_1 = 1.18x10^{13}\ m^{-3}$, $E_1 = 0.067$ eV and $A_2$=0.19 $m^2V^{-1}s^{-1}$ and $E_2$ =0.047 eV.

The polyimide films are not completely carbonized but partially carbonized. The partially carbonized polyimide is an n type donor. Since $A_1$=1.18x$10^{13}m^{-3}$, which is carrier density at infinite temperature and this correspons to the doner center density, which is about $10^{-14}$ times smaller than the number of molecules per $m^3$. That is only one part of $10^{-14}$ of the number of molecules become the doner centers. It is concluded this is not an intrinsic carriers but due to impurities. Therefor we can say that "the impurity level" lies about 0.134 eV below the conduction band.

4. CONCLUSIONS

Aromatic polyimide films were carbonized at 700 $^oC$ and 1000 $^oC$. The electrical conductivity was found to be $\sigma = \sigma_o \exp(-E / kT)$, $\sigma_o = 0.0125\ AV^{-1}m^{-1}$ and E= 0.02 eV. The Hall coefficient was negative, this implies that the carriers were electrons. Therefore, it was found that the carbonized film was an n type semiconductor or semi－metal. If the film is an n type semiconductor. The impurity level or valence band was found to be about 0.134 eV below the conduction band. At present, it is not clear whether the carbonized aromatic polyimide films are n type semiconductor or semi－metal. The mesurements of elctrical resistivitiy at low temperatures are in progress.

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