Polymer Bulletin 8, 117-124 (1982)

Polymer Bulletin

Hole Transport in Polyorganosilicon Thin Films

Jacek Tyczkowski, Jan Sielski and Marian Kryszewski

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
PL-90-362 Łódź, Poland

Summary

Hole transport in plasma - polymerized organosilicon films has been investigated. Measurements of the stationary conductivity dependence on temperature and applied electrical field and mobility determination by time of flight method were carried out. It was shown that holes can be transported either by states laying near or in the valence band, or by states near the Fermi level. The first transport mechanism dominates at about room temperature and above and the second one was found only in polysilazane at low temperature. Nitrogen containing structures are proposed as transport states near the Fermi level.

INTRODUCTION

The growing interest in the investigations of the structure and properties, mainly electrical and optical, of plasma polymerized organosilicon films is connected with the possibility of application of these films in micro - and optoelectronics. Polyorganosilicon films are easy to obtain, they have very good adhesion to substrates and high thermal resistance (KRYSZEWSKI et al. 1979). The uniform structure, high transparency in the visible region, smoothness of the surface and very small light losses (below 0.04 dB/cm) are indicating that they can be applied as thin films guiding light waves (TIEN et al. 1972). On the other hand, dielectric properties of these films are similar to silicon dioxide so they can be applied as passivators of semiconductor surfaces (MAISONNEUVE et. al. 1976).

The studies of electrical properties of polyorganosilicon thin films have shown that in these materials the bulk generation process (Poole - Frenkel mechanism) dominates in the electrical conduction (TYCZKOWSKI et. al. 1982). The investigations of "anomalous transient photocurrents" effect indicated that the generation centers are acceptors so the charge carriers involved are holes (TYCZKOWSKI and KRYSZEWSKI 1982). The analysis of the hole transport in these films is the subject of this paper.

According to the results of the studies of the hole and electron photoinjection from metal electrodes into these polymers (TYCZKOWSKI and KRYSZEWSKI 1981) and the optical absorption measurements we have suggested a general model of energy levels for organosilicon polymers (TYCZKOWSKI et al. 1981). Fig.1 illustrates this model. According to Mott's theory (MOTT and DAVIS 1971) and to our model one can see that the holes can be tran-

0170-0839/82/0008/0117/$01.60

sported either by states laying near or in the valence band, or by transport states near the Fermi level. In this paper it is shown that the first or the second transport mechanism can take place depending on the structure of the polymer film and the temperature.

EXPERIMENTAL

Thin polyorganosilicon films were prepared by plasma polymerization in the flow, electrode system. The current density of the glow discharge was 20 A/m^2 and frequency 20 kHz. Films obtained from hexamethyldisilazane (Si-N-Si) and hexamethyldisiloxane (Si-O-Si) were investigated. Stationary electrical conductivity measurements and mobility studies were carried out on films of the thick about 0.65 μm and 2.5 μm respectively, in the sandwich type systems.

Electrical conduction was measured in a shielded chamber by Takeda Riken TR 8641 electrometer using Keithley 240 A voltage supply. Conductivity was measured "step by step" at different temperatures. The polyorganosilicon thin films were prepared directly on glass supports (Corning 7059) with aluminium rear electrodes in glow discharge and then supplied with aluminium upper electrodes and guard rings.

Electron beam induced conductivity was studied for thicker polymer films (ten and more μm) e.g. by SUZUOKI et al. (1976) and YOSHINO (1978). For thin polymer films, in order to study the mobility of carriers by time of flight method it is necessary to choose such an energy of the electron beam and such a thickness of the upper electrode that the generation region can be neglected considering the sample thickness. In our mobility measurements the upper aluminium electrode was about 200 Å thick and the electron beam energy was 2 keV so the penetration depth was less than 0.2 μm. Intensity of the electron beam was chosen so that small signal conditions were preserved. Duration of electron pulses was 50 μs. The current transients were measured by a fast amplifier and recorded on oscilloscope.

Measurements of the optical absorption were made in the wavelength region from 185 to 350 μm using a Specord UV-VIS spectrometer, in nitrogen. In that case thin polyorganosilicone films were prepared on quartz plates.

RESULTS and DISCUSSION

The plots of current intensity dependence on reciprocal of temperature for polysiloxane and polysilazane thin films are shown in Fig.2. Both films show an activation relationship at room temperature and in the higher temperature range. This relation suggests that the transport of carriers is connected with transport bands i.e. transport states near or in the valence band. In the temperature range below room temperature the changes of electrical conductivity with temperature are different. The coductivity of polysiloxane drops below the measurement sensitivity while that of polysilazane films changes very slightly. The current intensity in polysilazane films is only twice smaller at liquid nitrogen than at room temperature. Such behaviour may indicate that the hopping transport by states near the Fermi level is involved.

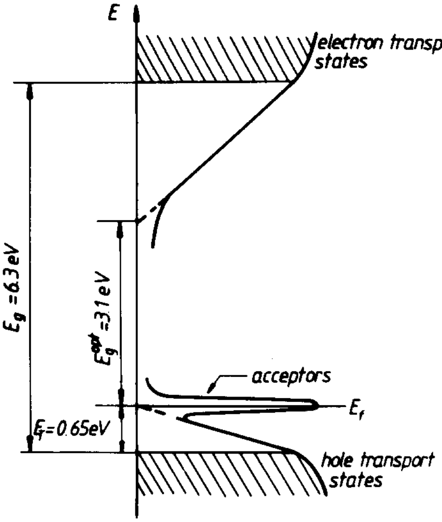

Fig.1. Scheme of energy level structure for plasma polymerized organosilicone films

Low temperature transport

Electrical conductivity in the case of the hopping transport through states near the Fermi level can be described by Mott's relation (MOTT and DAVIS 1971):

$$\sigma = \sigma'_0 \exp - (T_0/T)^{1/4} \quad (1)$$

The constants σ_0 and T_0 have the forms:

$$\sigma_0 = \sigma'_0 T^{-1/2} \quad (2)$$

and

$$T_0 \simeq 16 \frac{\alpha^3}{kN_E} \quad (3)$$

where: σ'_0 is a constant defined by Mott's theory, α is the inverse rate of fall-off of the wave function of a localized state, N_E is the density of states at the Fermi level and k is the Boltzmann's constant. Thus, relation (1) can be rewritten as follows:

$$\ln \sigma T^{1/2} = \ln\sigma'_0 - 2\left(\frac{\alpha^3}{kN_E}\right)^{1/4} \text{ x } T^{-1/4} \quad (4)$$

Plotting this relation in $\ln\sigma T^{12}$ vs T^{-14} coordinates we can estimate the density of states (N_E) from the slope of the obtained straight line.

Knowing the N_E value it is possible to estimate the average hopping distance (R) and the average hopping energy (W) at a given temperature:

$$R = \left(\frac{9}{8\pi\alpha kTN_E} \right)^{1/4} \quad (5)$$

and

$$W = \frac{3}{4\pi R^3 N_E} \quad (6)$$

Fig.3 presents the plot of $\ln\sigma T^{1/2}$ vs $T^{-1/4}$ for polysilazane film. The straight line dependence for low temperature region supports the conclusion that, for this film, relation (4) is fulfiled. The parameters describing hopping transport which were calculated for 150°K (temperature upper limit where the low temperature hopping mechanism is still visible) from the slope of straight line, taking $\alpha = 10^7$ cm^{-1} (SAHA et al 1976, AUGELLI et al. 1980), are: $N_E \simeq 3\text{x}10^{21}$ cm^{-3} eV^{-1}, $R \simeq 17$ A and $W \simeq 0.02$ eV. If, as sugested by MOTT and DAVIS (1971) the transport states near Fermi level are confined to a band of width about 2W, then the space density of these states is at least 10^{20}cm^{-3}. This value is by two orders of magnitude higher in comparison with the determined space density of the of the specific acceptor

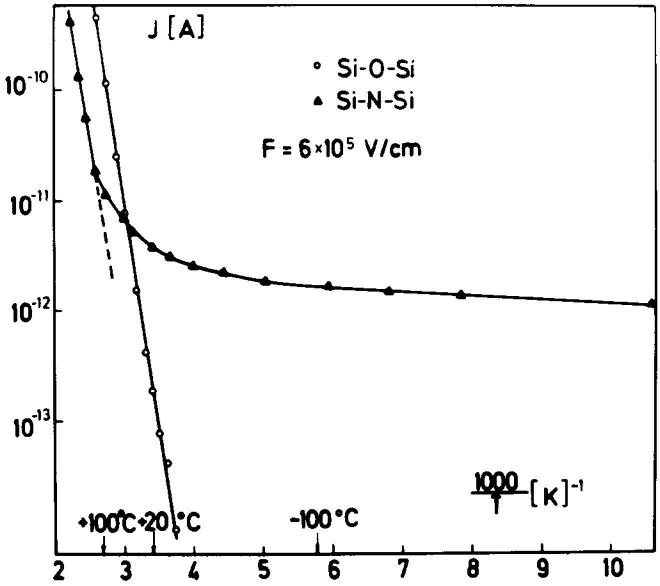

Fig. 2. Current intensity dependence on reciprocal temperature for polysiloxane and polysilazane

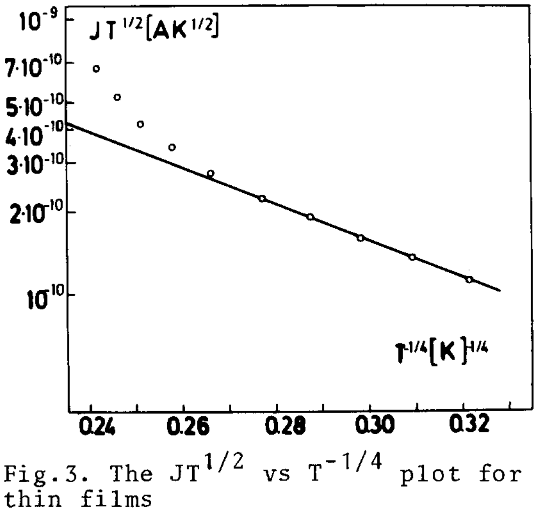

Fig.3. The $JT^{1/2}$ vs $T^{-1/4}$ plot for polysilazane thin films

centers (TYCZKOWSKI and KRYSZEWSKI 1982) both in polisilazane and polisiloxane. Taking into consideration the energy diagram (Fig.1) one can see, that the hopping states and the acceptor centers have similar energies i.e. they are situated near the Fermi level. Such a position of the hopping states enables the low temperature hopping process.

This conclusion concerning the energetical position of the hooping states is further supported by the results of the optical absorption measurements. Fig.4 shows the absorption spectra of the studied polymer films and corresponding monomers. The long absorption tails in the spectra of polymers has been ascribed to localized states according to Mott's theory (MOTT and DAVIS 1971). It was shown that for absorption coefficient $\alpha > 10^4$ cm^{-1} this tails can be described by the cubic dependence (TYCZKOWSKI et al.1981):

$$\alpha h\nu \sim (h\nu - E_g^{opt})^3 \qquad (7)$$

where E_g^{opt} is the optical gap interpreted as in Fig.1. Dashed lines in Fig.4 represent the relation (7) and fit well the experimental spectra. However, it can be seen that the lack of fitting appears for the polysilazane film in the range of higher energy than for the polysiloxane film. The region of this deflection agrees with the monomer absorption maximum. It my indicate that the monomer absorption band appears for polymer too. The distance between monomer absorption maximum and the maximum of fundamental absorption band in the polymer (connected with electronic transitions between the transport bands) is about 0.5 eV. It means that the states connected with absorption band which corresponds to monomer absorption maximum are situated near the Fermi level (see Fig.1). One can conclude that these states are responsible for low temperature hopping.

The fact that the low temperature hopping near the Fermi level occurs in polysilazane films and is not observed in polysiloxane films indicates probably of the role of nitrogen containing structures, which are present in polysilazanes and absent in polysiloxanes, as the hopping centers.

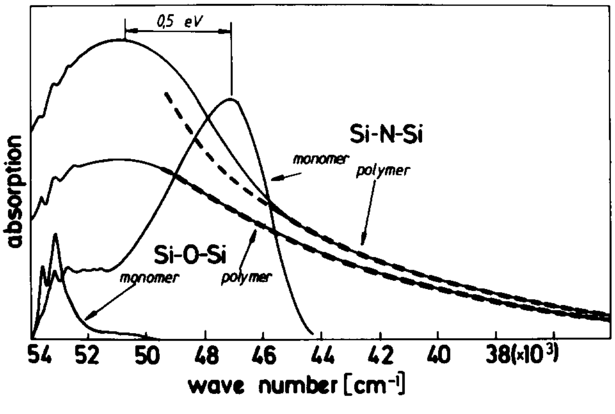

Fig.4.Absorption spectra of polysilazane and polysiloxane and for the corresponding monomers. The dashed lines are the curves calculated according to eq. (7)

High temperature transport

Now, we return to higher temperature transport which take place near or in the valence band. The estimation of the hole mobility μ is the first step in the study of this process. It was done in two different ways. First - the μ value was evaluated from measurements of stationary electrical conduction, and second - using the time of flight method. This analysis concerns polysiloxane thin films because they exhibit only one type of carrier transport. For polysilazane thin films similar behaviour can be expected because a parallel straight line in the Fig.2 is characteristic for this material too.

Stationary electrical conductivity

The stationary electrical conductivity in the thin polysiloxane films can be described by Poole - Frenkel relation (SIMMONS 1971):

$$\sigma=\sigma_o \exp \quad (\beta F^{12}-E_A)/kT \qquad (8)$$

where: $\sigma_o=e\mu N_o$ (9)

E_A is the activation energy, F is the applied field, β is the Poole - Frenkel coefficient, N_o is the density of generation centers and e is the electron charge. Plotting $\ln\sigma$ vs F^{12} and knowing the E_A value we can calculate σ_o values. Fig.5 shows this plot for polysiloxane film. In this case E_A=0.65 eV and σ_o is about 2×10^{-6} Ω cm $^{-1}$. With the density of generation centers, which we have determined from "anomalous transient photocurrent" effect (TYCZKOWSKI and KRYSZEWSKI 1982) being equal to 10^{18} cm^{-3}, one can estimate the hole mobility $\mu \simeq 3 \times 10^{-6}$ cm^2/Vs for F → 0.

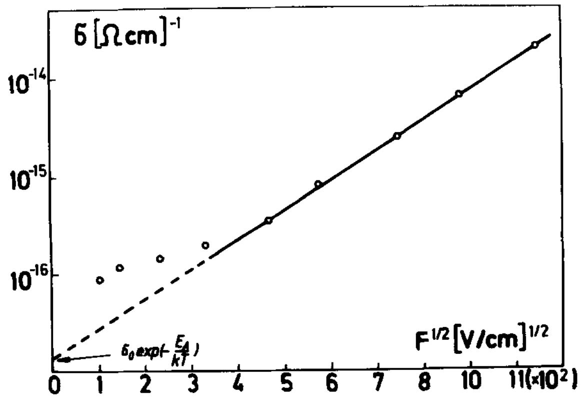

Fig.5. Poole - Frenkel plot (lg σ vs F^{12}) for polysiloxane

Mobility measurements

For mobility determination we have applied time of flight method using pulsed electron beam excitation. The short pulse of electron beam generates hole - electron pairs in thin layer of polymer film which result in a transient current due to the application of external electrical field with appropriate polarization.

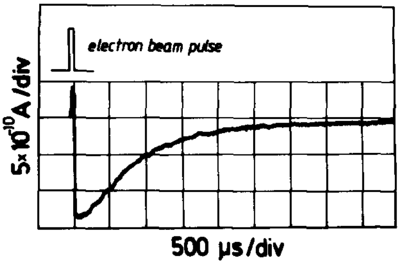

Fig.6 Current transient in a thin polysiloxane film. Applied voltage 120 V

Fig.6 presents a hole current transient induced by electron beam pulse. Monotonous decrease of the current suggests the dispersive transport of holes. Thus, we can describe carrier transport by Scher-Montroll theory (SCHER and MONTROLL 1975). According to this theory, the current (j) decay can be described by exponential functions:

$$j \sim t^{-(1-\alpha)} \quad \text{for } t < t_T$$

$$j \sim t^{-(1+\alpha)} \quad \text{for } t > t_T \qquad (10)$$

and $0 < \alpha < 1$

where t_T is interpreted as the transit time of the carrier front and α is a parameter describing the degree of the dispersion. The hole current transient from fig.6 plotted in the Scher - Montroll system is presented in fig.7. The α values, which were estimated from the slopes of both straight lines are similar (about 0.8) and the sum of the slopes is about 2, consistently with the theory of Scher - Montroll.

The carrier mobility can be calculated as follows:

$$\mu = \frac{d^2}{t_T V} \qquad (11)$$

where V is the applied voltage and d is the film thickness.

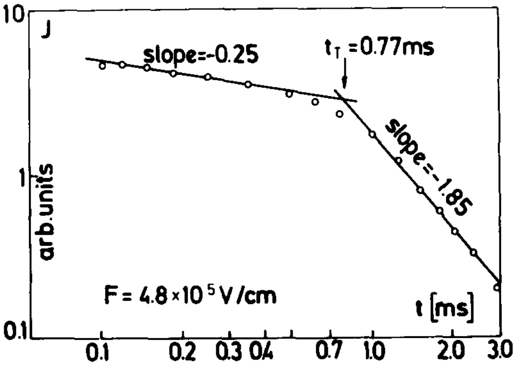

Fig. 7 Scher - Montroll plot for transient hole current in thin polysiloxane film

The time of flight experiments show a small decrease of μ values with increasing applied voltage. It is inconsistent with Scher - Montroll expectation but this behaviour was already found for the some amorphous materials with dispersive transport (YOSHINO et al. 1978). Exrapolating the values of mobility to V=0 we obtained $\mu=3.5 \times 10^{-6}$ cm^2/Vs. This result is in agreement with the value of mobility obtained from stationary conductivity measurements.

CONCLUSIONS

The transport of holes, originated from dissociation of acceptor centers, occurs in polyorganosilicon films involving transport states situated near or in the valence band. The values of hole mobility, estimated from the stationary conductivity measurements and calculated from time of flight measurements are identical and equal to 3×10^{-6} cm^2/Vs. It seems that holes are transported in the same way as well in stationary as in pulse conductivity. The activated character of the hole generation process causes that the stationary conductivity and thus stationary charge transport for the materials under study clearly appears at about room temperature and above it.

The presence of the nitrogen containing structures in polysilazanes probably involves the appearance of a band of states near the Fermi level. These states are responsible for the low temperature hopping transport in polysilazane films.

The determination of the molecular structures connected with the transport states in thin films of polyorganosilicones is the aim of the work in progress.

References

AUGELLI, V., MURRI, R., GALASSINI, S., and TEODORE, A.: Thin Solid Films 69, 315 (1980)

KRYSZEWSKI, M., WROBEL, A.M., and TYCZKOWSKI, J.: Plasma Polymerization, Washington: ACS Symp., Ser. 108, pp 219-36 (1979)

MAISONNEUVE, M., SEGUI, Y., and BUI, A.: Thin Solid Films 33, 35 (1976)

MOTT, N.F., and DAVIS, E.A.: Electronic Processes in Non-Crystalline Materials, Oxford: Clarendon Press 1971

SAHA, K., ABBI, S.C., and POHL, H.A.: J.Non-Cryst. Solids 21, 117 (1976)

SCHER, H., and MONTROLL, E.W.: Phys. Rev. B12, 2455 (1975)

SIMMONS, J.G.: J.Phys. D: Appl.Phys.4, 613 (1971)

SUZUOKI, Y., MIZUTANI, T., and IEDA, M.: Japan, J.Appl.Phys. 15, 1665 (1976)

TIEN, P.K., SMOLINSKY, G., and MARTIN, R.J.: Appl. Opt. 11, 637 (1972)

TYCZKOWSKI, J., CZEREMUSZKIN, G., and KRYSZEWSKI, M.: Materials Sci. 7, 371 (1981)

TYCZKOWSKI, J., CZEREMUSZKIN, G., and KRYSZEWSKI, M.: phys. stat. sol., in press (1982)

TYCZKOWSKI, J., and KRYSZEWSKI, M.: J.Phys.D: Appl.Phys. 14, 1877 (1981)

TYCZKOWSKI, J., and KRYSZEWSKI, M.: Appl. Phys.Lett., submitted to editor (1982)

YOSHINO, K., KYOKANE, J., NISHITANI, T., and INUISHI, Y.: J.Appl. Phys. 49, 4849 (1979)

Received June 21, accepted after revision August 13, 1982 C