

The Electrical Conductivity of Polysilane, $(\text{SiH}_2)_x$

Phillip John, Ibrahim M. Odeh, and John Wood

Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS, U.K.

The d.c. electrical conductivity of polysilane, $(\text{SiH}_2)_x$, as compressed discs, has been measured at 298 K; values of the conductivity lie in the range 10^{-7} – $10^{-11} \Omega^{-1} \text{cm}^{-1}$ for pristine samples of polysilane.

Considerable interest has recently been shown in the synthesis and properties of semiconducting polymers such as $(\text{SN})_x$ ¹ and $(\text{CH})_x$.² The conjugative ability of the Si–Si covalent bond is well established.^{3,4} Evaluation of new anisotropic conductors led us to investigate potential non-metallic materials of high conductivity based on catenated silicon polymers. We have synthesised⁵ a high molecular weight polysilane, $(\text{SiH}_2)_x$, as an air-sensitive orange solid. Details of the method based on the Li reduction of SiH_3Cl_2 in scrupulously dried tetrahydrofuran have been reported elsewhere.⁶ Characterisation of the polysilane by i.r. spectroscopy,^{6,7} Raman scattering,⁸ and elemental analysis is consistent with an empirical formula $(\text{SiH}_2)_x$.

Because polysilane is easily oxidised all manipulations and measurements were performed *in vacuo* or in an Ar atmosphere (<1 p.p.m. O_2 , <150 p.p.m. H_2O). Compacted discs (13 mm diameter, 0.5–0.8 mm thickness) of polysilane were prepared in an hydraulic press (0.16 kg m^{-2}). The discs were sandwiched between two polished copper electrodes encased in a perspex holder. D.c. conductivities of the samples, in an Ar atmosphere, were measured with a picoammeter interfaced with a mini computer. The I – V characteristics were obtained at 2 V increments increasing the applied voltage from 2 to 30 V and subsequently reducing it from 30 to 2 V. Current measurements were taken 5 min after each voltage increment. The current did not change with time at a constant applied voltage. A representative set of readings is shown in Figure 1; each datum point is an average of three readings. The standard deviation is estimated to be <1%. Electrical contacts made by Ag conducting paint (Electrodag) did not alter, within experimental error, the measured conductivities. Room temperature conductivities are reported as $\sigma \equiv L/RA$ where L is the thickness, R the resistance, and A the cross sectional area. Values of R were obtained from the linear portions of I – V graphs at voltages greater than 20 V. The conductivities of ten samples were independently measured and lay in the range 10^{-7} – $10^{-11} \Omega^{-1} \text{cm}^{-1}$ at 298 K. The conductivities measured with the present experimental arrangement are subject to uncertainties due to junction potentials. The I – V curves of all the samples exhibited two common features as

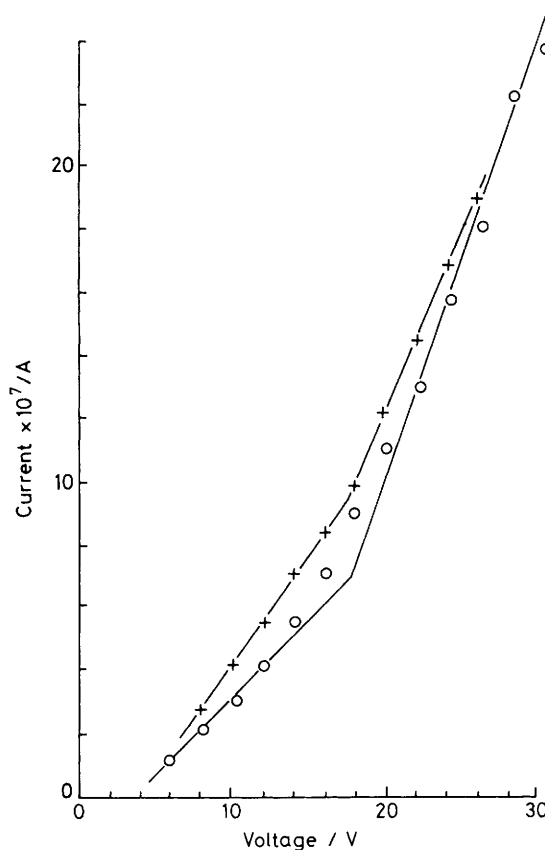


Figure 1. I – V characteristics of polysilane, $(\text{SiH}_2)_x$, as a compressed disc (13 mm diameter, 0.61 mm thickness) under an Ar atmosphere. \circ = increasing voltage; + = decreasing voltage.

exemplified by the data in Figure 1. First, a distinct break in the slope was observed at *ca.* 20 V on both increasing and decreasing the applied voltage. To differing degrees, hysteresis

was present in each I - V curve. Secondly, curvature was evident in the I - V plots at voltages <5 V giving rise to apparent intercepts in the I - V graphs. The conductivity of pristine polysilane appears to be electronic in character. No evidence of any measurable increase in the resistance of the films was observed after the passage of a d.c. current sufficient for complete polarisation if ionic conduction were operative.

We note, for comparison, that the intrinsic room temperature conductivity of crystalline films of polyacetylene varies from $10^{-5} \Omega^{-1} \text{cm}^{-1}$ for *trans*-(CH) $_x$ to $10^{-9} \Omega^{-1} \text{cm}^{-1}$ for the *cis*-isomer.⁹ In view of the sensitivity of the conductivity of polyacetylene² to impurities and/or defects it is prudent to assume the intrinsic conductivity of pure polyacetylene is even lower. Polysilane is susceptible to oxidation¹⁰ and hence, resistive oxide barriers at the Cu-polysilane interface may lead to an increase in the resistivity.

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