The Electrical Conductivity of Polysilane, $(SiH_2)_x$

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The d.c. electrical conductivity of polysilane, $(SiH_2)_x$, as compressed discs, has been measured at 298 K; values of the conductivity lie in the range 10^{-7}—10^{-11} Ω^{-1} cm^{-1} for pristine samples of polysilane.

Considerable interest has recently been shown in the synthesis and properties of semiconducting polymers such as $(SN)_x$[1] and $(CH)_x$.[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 synthesised[5] a high molecular weight polysilane, $(SiH_2)_x$, as an air-sensitive orange solid. Details of the method based on the Li reduction of SiH_2Cl_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 $(SiH_2)_x$.

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} Ω^{-1} 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

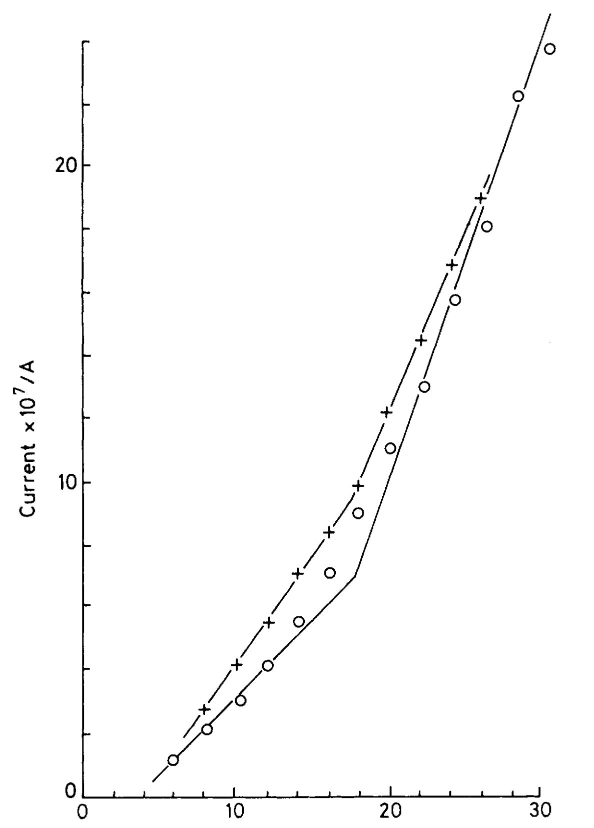

Figure 1. *I–V* characteristics of polysilane, $(SiH_2)_x$, as a compressed disc (13 mm diameter, 0.61 mm thickness) under an Ar atmosphere. ○ = increasing voltage; + = decreasing voltage.

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 $10^{-5}\,\Omega^{-1}\,cm^{-1}$ for *trans*-$(CH)_x$ to $10^{-9}\,\Omega^{-1}\,cm^{-1}$ for the *cis*-isomer.[9] In view of the sensitivity of the conductivity of polyacetylene[2] to impurities and/or defects it is prudent to assume the intrinsic conductivity of pure polyacetylene is even lower. Polysilane is susceptible to oxidation[10] and hence, resistive oxide barriers at the Cu–polysilane interface may lead to an increase in the resistivity.

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