PREPARATION AND PROPERTIES OF POLYSILANES : MODEL COMPOUNDS FOR HYDROGENATED α -Si

P. John, I. Odeh, M. Thomas, J. Wilson

► To cite this version:

P. John, I. Odeh, M. Thomas, J. Wilson. PREPARATION AND PROPERTIES OF POLYSILANES : MODEL COMPOUNDS FOR HYDROGENATED α -Si. Journal de Physique Colloques, 1981, 42 (C4), pp.C4-651-C4-654. 10.1051/jphyscol:19814143 . jpa-00220764

HAL Id: jpa-00220764

<https://hal.science/jpa-00220764>

Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

PREPARATION AND PROPERTIES OF POLYSILANES : MODEL COMPOUNDS FOR HYDROGENATED a-Si

P. John, I.M. Odeh, M.J.K. Thomas and J.I.B. Wilson*

Department of Chemistry,

**Department of Physics,*

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

Abstract The infrared and electronic spectra of hydrogenated polysilanes, of approximate composition $-(SiH_2)_n-$ and $-(SiH)_n-$ have been compared to hydrogenated a-Si. An investigation of the oxidative stability of films of these materials by infrared spectroscopy has been used to interpret 'ageing' phenomena exhibited by certain glow-discharge a-Si films prepared at high r.f. powers (>100W).

- 1. Introduction** An understanding of the role of polysilane chains, notably $-(SiH_2)_n-$, is important in elucidating the structure of certain hydrogenated amorphous silicon films. The presence of $-(SiH_2)_n-$ has been inferred [1] from the 840 cm^{-1} band which may be assigned to the b_{1u} wagging vibration † of the entire chain when $n \geq 2$. Such catenates have been implicated [2] as an integral part of the hydrogen-rich phase in a-Si films exhibiting 'columnar' morphology [3] and may be responsible for their poor oxidative stability. Isothermal dehydrogenation studies [4] of r.f. a-Si films demonstrate that $-(SiH_2)_n-$ chains are degraded rapidly at ca. 350°C and this process has been tentatively associated with striated fractures [5] peculiar to r.f. films prepared at low substrate temperature.

Notwithstanding the importance of such material as model compounds for structural entities in a-Si, linear chain polysilanes, $-(SiH_2)_n-$, are potential precursors to one dimensional semiconductors and offer the prospect for an alternative, chemically based, route to a-Si.

- 2. Preparation** Dichlorosilane, SiH_2Cl_2 , was reacted in vacuo with granular Li suspended in rigorously dried tetrahydrofuran at room temperature. The initial mole ratio of Li : SiH_2Cl_2 was 20 : 1 for the present results. An air-sensitive orange/yellow solid was deposited of approximate composition $-(SiH_2)_n-$ (vide infra). Similarly a brown material, $-(SiH)_n-$, was synthesised from the Li reduction of trichlorosilane, $SiHCl_3$, in tetrahydrofuran.
- 3. Characterisation**
 - 3.1. Infrared Spectroscopy** The ir transmission spectra of $-(SiH_2)_n-$ and $-(SiH)_n-$, dispersed in a nujol mull, are shown in figure 1. Two features of the spectra are of import to the interpretation of the ir spectroscopy of hydrogenated a-Si. First, the unresolved symmetric (b_{3u}) and asymmetric (b_{2u}) silicon-hydrogen stretching modes of $-(SiH_2)_n-$ occur with a band maxima at 2100 cm^{-1} . In

†

we adopt a D_{2h} line group symmetry for $-(SiH_2)_n-$.

contrast $-(\text{SiH})_n^-$ exhibits a stretching mode at 2000 cm^{-1} . Secondly, a characteristic doublet occurs for $-(\text{SiH}_2)_n^-$ in the bending region at 905 cm^{-1} and 850 cm^{-1} ; these bands are assigned to the bending (ν_{2u}) mode of SiH_2 groups and the wagging (ν_{1u}) mode of an extended polysilane $-(\text{SiH}_2)_n^-$ chain.

Fig. 1

Infrared transmission spectra
of $-(\text{SiH}_2)_n^-$ (a) and $-(\text{SiH})_n^-$ (b)

3.2. Electronic Spectroscopy Electronic spectra, in the range 200 - 800 nm, of the solution during the synthesis of $-(\text{SiH}_2)_n^-$ were obtained. Prior to solid deposition the solution gave rise to two absorption bands exhibiting differing characteristics. The shorter wavelength component remained constant in intensity and position (255 nm) during the course of the reaction. The second absorption band, observed initially at 295 nm, shifted to longer wavelengths with time until attaining a limiting cut-off value at 400 nm prior to solid deposition. Furthermore, the intensity of the latter band increased markedly with increasing wavelength of the band maximum. A comparison of the spectra of the polysilane solution with that of r.f. a-Si is shown in figure 2. For

Fig. 2

Electronic spectra of
partially oxidised
 $-(\text{SiH}_2)_n^-$ sample (a),
 $-(\text{SiH}_2)_n^-$ (b) and
an r.f. a-Si film (c).

linear substituted silicon catenates, the absorption frequency, ν , is given by the simple Hückel molecular-orbital expression [6]

$$h\nu = \alpha_{\text{Si}} + 2\beta_{\text{SiSi}} \cos(2\pi/n + 1)$$

where α_{Si} , β_{SiSi} are constants and n is the chain length. Employing the former constants established for α,ω -polysilanes the dependence of ν on chain length may be estimated and the results demonstrate that $n > 20$. It is to be noted that branched substituted polysilanes do not exhibit frequency shifts on conjugation [6].

3.3 Oxidative Stability

3.3.1. Polysilane The ir transmission spectra of both materials, $-(\text{SiH}_2)_n-$ and $-(\text{SiH})_n-$, were measured after exposure to moist air. Oxidation was rapid under these conditions as indicated by the pronounced changes to the ir and electronic spectra (figures 2 and 3). A series of distinct bands in the silicon-hydrogen stretching region were produced on oxidation arising from

Fig. 3a Infrared transmission spectra of partially oxidised $-(\text{SiH})_n-$ (a) and $-(\text{SiH}_2)_n-$ (b). Curve (c) corresponds to a sample of $-(\text{SiH}_2)_n-$ subject to extensive oxidation.

Fig. 3b Linear relationship between the band maxima and the electro-negativity sum $\sum \text{SR}(\text{R})$. ●, $=\text{SiH}$; ○, $=\text{SiH}_2$ derived from data of fig. 3a. □, H implanted SiO_2

$=\text{SiH}$ or $=\text{SiH}_2$ groupings contiguously bound to one or more oxygen atoms [7]. The systematic increase in the wavenumber of the band maxima have been associated with the number and type of electronegative element bound to the silicon-hydrogen groupings [8]. The wavenumber of the peak maxima are plotted in figure 3 as a function of $\sum \text{SR}(\text{R})$ where SR is a measure of the electro-negativity of the neighbouring atom R and the sum is taken over the nearest neighbours. Each band in figure 3 can be thus associated with a particular microenvironment around the absorbing group.

Confirmation that oxidation of these materials proceeded via silicon-silicon bond fission was demonstrated by electronic spectroscopy. On exposure of the polysilane $-(\text{SiH}_2)_n-$ to air the colour changes rapidly from orange/yellow to white as silicon-silicon conjugation was reduced. The effect is shown in figure 2 where the dashed line is the absorption spectrum of a polysilane solution exposed to oxygen.

3.3.2. Glow-discharge a-Si Certain r.f. films prepared at high powers ($>100\text{W}$) undergo oxidation when exposed to atmospheric air as shown by the development of distinctive ir bands (figure 4). The growth of bands at wavenumbers identical to those previously measured in oxidised polysilanes can be unequivocally assigned to structural groupings defined in 3.3.1.

Fig. 4. Infrared transmission spectra of a high power (100W) a-Si film as a function of the time of exposure to laboratory air.

4. Conclusion The chemical synthesis of $-(\text{SiH}_2)_n-$ and subsequent characterisation aids the ir band assignments of hydrogenated a-Si films. Furthermore, comparison of the ir spectra of oxidised $-(\text{SiH}_2)_n-$ and a-Si allow a detailed molecular explanation of the 'ageing' of glow 2n discharge a-Si films prepared at high powers.

References.

1. KNIGHTS, J.C., LUCOVSKY, G. and NEMANICH, R.J., *Phil.Mag.B*, **37**(1978)467.
2. KNIGHTS, J.C. and LUCOVSKY, G., *CRC Critical Reviews in Solid State and Material Sciences*, **9** (1980)211.
3. KNIGHTS, J.C., LUCOVSKY, G. and NEMANICH, R.J., *J.Non-cryst.Solids*, **32** (1979)393.
4. JOHN, P., ODEH, I.M., THOMAS, M.J.K., TRICKER, M.J., RIDDOCH, F. and WILSON, J.I.B., *Phil. Mag.B*, **42** (1980)671.
5. JOHN, P., ODEH, I.M., THOMAS, M.J.K., TRICKER, M.J., WILSON, J.I.B. and DHARIWAL, R.S., *J.Mat.Sci.*, **16**(1981)1305.
6. RHEINGOLD, A.L. (ed) 'Homocyclic Rings, Chains and Macromolecules,' Elsevier, 1977.
7. JOHN, P., ODEH, I.M., THOMAS, M.J.K., TRICKER, M.J. and WILSON, J.I.B., *Phys.Stat.Sol.*, in press.
8. LUCOVSKY, G., *Sol.State Comm.*, **29**(1979)571.