The Interaction of Tetramethylsilane with an Electron-emitting Tungsten Filament

By M. W. ROBERTS* and J. R. H. ROSS

(*School of Chemistry, The University of Bradford, Bradford* 7)

Summary Tetramethylsilane interacts with a hot tungsten filament to give mainly $H_{2(g)}$ and $CH_{4(g)}$ and incorporation of C and Si into the filament; this reaction is field-dependent and under certain conditions negative ions form.

POLYMER film formation by electron bombardment techniques has been reported to occur by a number of different mechanisms. Christy[1] suggests that the polymerisation of the siloxane pump oil, DC 704, depends on the rate at which adsorbed molecules are bombarded by electrons to form free radicals which subsequently polymerise; on the other hand, Haller and White[2] conclude that in the polymerisation of butadiene, the rate depends on the reaction of monomer molecules with sites created on the surface by electron bombardment. In this work, we have investigated the interaction of tetramethylsilane, $SiMe_4$, with an electron-emitting tungsten filament; $SiMe_4$ was chosen because of its molecular simplicity and because of its similarity to siloxanes used commercially for the formation of polymer films.

The reaction was investigated using a flow system (pressures from 10^{-5}—10^{-2} torr, 1 torr = 133·3 Nm^{-2}) with mass-spectrometric analysis to determine the rate and stoicheiometry of reaction. The filament was several centimetres of 0·2 mm diameter tungsten wire and a voltage (0—250 v positive) was applied to a tungsten ribbon which could be positioned between 0·1 and 3 cm from the filament; a spacing of 1 cm was used in typical experiments.

Without an applied voltage and with filament temperatures in the range 1700—2200 K, the main gaseous products were hydrogen and methane with traces of ethylene; the stoicheiometry of the reaction, neglecting C_2H_4, conforms to equation (1). Simultaneous measurements of the resistance of the tungsten filaments[3] indicated that extensive incorporation of carbon and possibly silicon was occurring.

$$n\mathrm{Si(CH_3)_{4(g)}} \rightarrow (\mathrm{SiC_{3\cdot8}})_{n(\mathrm{ads})} + 5{\cdot}6n\mathrm{H_{2(g)}} + 0{\cdot}2n\mathrm{CH_{4(g)}} \qquad (1)$$

When a gradually increasing voltage was applied between the ribbon and filament, the rate of reaction was found to increase rapidly at about 20 v. Below this voltage, which we term the *critical voltage* V_C, the emission current I was negligible compared with the emission current in vacuum I_e, but it rose concurrently with the rise in the rate of reaction (see Figure). Above V_C, the stoicheiometry was given by equation (2). Growth of a polymer film with

$$n\mathrm{Si(CH_3)_{4(g)}} \rightarrow (\mathrm{SiC_{3\cdot3}H_{7\cdot2}})_{n\mathrm{(ads)}} + 1{\cdot}4n\mathrm{H_{2(g)}} + 0{\cdot}3n\mathrm{CH_{4(g)}} + 0{\cdot}2n\mathrm{C_2H_{4(g)}} \qquad (2)$$

insulating properties was observed on the ribbon during reaction above V_C; as in all cases the rate of reaction above V_C was very much greater than below, the rate of the carbiding/siliciding reaction is negligible compared with the polymerisation reaction, and equation (2) corresponds to the stoicheiometry of the latter, indicating that silicon, carbon, and hydrogen are all incorporated in the polymer film. Using a magnetron,[3] the rate of reaction above V_C has been shown to be very close to the rate, $\frac{dN}{dt}$, of formation of negative ions from $\mathrm{SiMe_4}$ at a tungsten filament. Hence, we conclude that above V_C, the reaction is the formation of negative ions at the emitting surface, and that these ions are accelerated towards the anode, where they polymerise.

Evidence for the mechanism of the ionisation process was obtained by examining the dependence of V_C on $\mathrm{SiMe_4}$ pressure (P) and on the inter-electrode spacing. The critical voltage at any pressure was found to be directly dependent on the spacing, suggesting that the relevant parameter is the *field* at the surface rather than the voltage. It can be shown[4] that this is consistent with equation (3) which describes the rate of desorption of negative ions from

$$\frac{dN^-}{dt} = A_{\theta,\epsilon} \exp \frac{e(S - \phi_\theta + \sqrt{e\epsilon})}{kT} \qquad (3)$$

a surface at temperature T with an applied field ϵ. A is a pre-exponential term which depends on ϵ as well as the coverage θ of the surface by reacting species, S is a term which includes the electron affinity of this species, its heat of adsorption, *etc.*, ϕ_θ is the work function of the surface at coverage θ (increases with increasing θ), k is the Boltzmann constant, and e is the charge on an electron. The Schottky term $\sqrt{e\epsilon}$ allows for the decrease in the energy barrier when a field is applied. In essence, the phenomena shown in the Figure and the existence of the critical field observed in the present work can be explained by the following sequence of events:—

(i) Below ϵ_C, the critical field, negative ion formation is negligible and the adsorbed species decompose to give carbides/silicides. The coverage θ is determined by P.

(ii) As the field is increased, the term $\sqrt{e\epsilon}$ in equation (3) increases until at ϵ_C negative ions are formed. The field then determines the coverage, which decreases, with a consequent decrease in ϕ_θ towards the clean metal value. The activation energy term in equation (3) is thus decreased considerably and there is a corresponding increase in the term $A_{\theta,\epsilon}$. Hence, a large increase in the negative ion current occurs with only a small increase in the applied field; there is a simultaneous rapid rise in electron current due solely to the drop in ϕ_θ. The rate-determining step in this region is desorption of negative ions.

(iii) When the negative ion current, and hence the rate of reaction, increases, the pressure drops. A situation is soon reached with increasing field when the rate of supply of $\mathrm{SiMe_4}$ becomes rate-determining, andthis results in the flattening off of the rate (Figure).

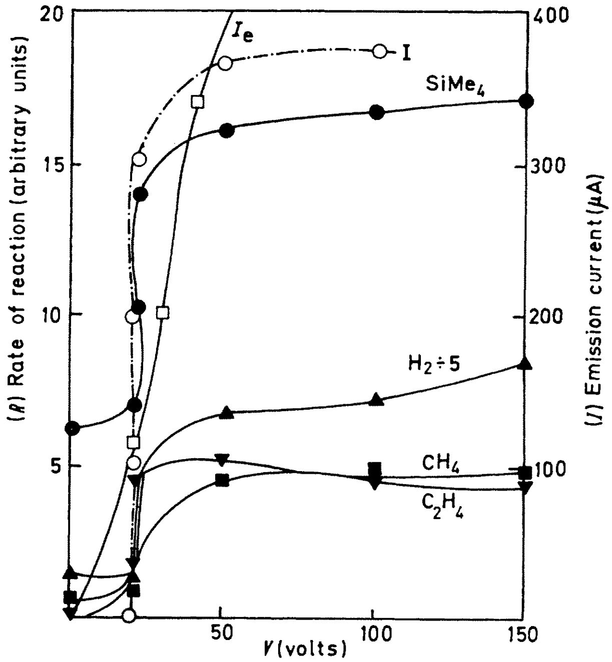

FIGURE. *Effect of voltage* V *on the rate of reaction* R *and the emission current* I *at a filament temperature of* 1980K; *rate of disappearance of* $\mathrm{SiMe_4}$, ●; *rate of appearance of* $\mathrm{H_2}$ (÷ 5), ▲; $\mathrm{CH_4}$, ■; $\mathrm{C_2H_4}$, ▼; *total emission current,* I, ○; *vacuum emission current,* I_e, □.

These results show that negative ions formed at the emitting surface play an important part in the polymerisation of organic molecules by the electron-beam polymerisation process. Such a process is most efficient for monomers with high electron affinities and low heats of adsorption and with low-work-function emitters.

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