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# Studies on the reaction between silane and hydrogen peroxide vapour; surface formation of planarized silica layers

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The chemistry of the reaction of gaseous silane with hydrogen peroxide vapour at low pressure, which yields commercially valuable planarized silica layers on line-etched silicon wafers, has been studied for the first time. Monitoring the mixed vapours by line-of-sight mass spectrometry and by low temperature infrared spectroscopy together with deuteriation and quantification studies indicates the reaction occurs only on surfaces, probably by a free radical mechanism. The conditions which allow the formation of self-planarizing, 'flowy' silica films are consistent with a sol–gel process. It was found that hydroxyl radicals, formed in this work by microwave dissociation of water vapour, react in the gas phase with silane to give silica films which do not form planar layers on line-etched wafers.

It is evident from the well known chemical properties of the two molecules $SiH_4$ and $H_2O_2$ that they must react under some conditions to give silica as one reaction product. However, the reaction between silane and hydrogen peroxide vapour seems to have been studied previously only in relation to a commercial process developed by Electrotech.[1,2] This company has shown that when silane is mixed with an excess of hydrogen peroxide vapour (formed by flash vaporization of >30% $H_2O_2$) at low pressure, silica is formed on adjacent surfaces. Under optimized conditions of pressure and temperature, the silica layer flows to mask irregularities on the surface giving a planarized layer. These 'flowy' films are of importance in the electronics industry for gap filling and covering the line-etched patterns of silicon based electronic devices with an electrically insulating layer. Such effective planarization with good gap filling properties is not easily obtained directly by more usual processes such as plasma deposition or spin coating with liquid precursors of silica.[3]

In this paper we report on a chemical study of the $SiH_4$ and $H_2O_2$ vapour reaction leading to silica film formation and attempts to reveal some aspects of its mechanism.

## Results

The apparatus shown in Fig. 1 was used for obtaining flowy silica films on a convenient laboratory scale. Liquid hydrogen peroxide (30–90%) was drawn into an evacuated flash evaporator and the vapour was mixed with $SiH_4$ as it left a concentric nozzle system. Initially, the mol ratio $SiH_4 : H_2O_2$ was 1 : 10 and typically 0.7 mmol $SiH_4$ was used in a run lasting *ca.* 2 min. Silica was deposited on a target/window consisting of a cooled silicon wafer mounted within an infrared cell as shown. The pressure in the deposition region was within the range 0.6–1.3 hPa and the window was at 5–10 °C (at higher temperatures the films were not flowy). When the run was complete, the cell was evacuated to a pressure <1 Pa. As discussed below, the time of pumping affected the residual water content of the film.

Using line-etched silicon wafers as deposition targets and subsequent inspection by optical and scanning electron microscopy, it could be seen that the deposits were flowy giving planarized layers with good gap filling qualities like those reported earlier.[1,2]

The infrared spectrum of a silica layer deposited on the silicon window is shown in Fig. 2(*a*). The size of the ν(OH) band at around 3300 and the much weaker δ(OH) band at 1630 $cm^{-1}$ varied from run to run depending on the time the film had been pumped on under high vacuum but the 1630 $cm^{-1}$ peak virtually disappeared after 45 min pumping. The largest peak in all the spectra was the ν(SiO) band at 1083 $cm^{-1}$. The band at 795 $cm^{-1}$ seems equivalent to the 800–810 $cm^{-1}$ peak found in the spectra of anhydrous, densified silicas[4] but the peak at 930 $cm^{-1}$ is associated with silica containing Si–OH groups.[5] Treatment of the film on the window with the vapour of hexamethyldisilazane followed by brief pumping under high vacuum caused the 930 $cm^{-1}$ peak and most of the 3300 $cm^{-1}$ to disappear as shown in Fig. 2(*b*) but this treatment caused no changes to the 1083 and 795 $cm^{-1}$ peaks.

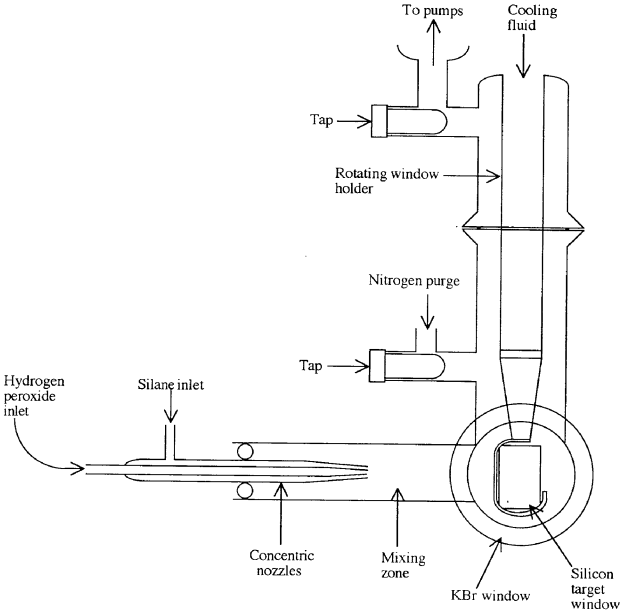

**Fig. 1** Apparatus for silica film deposition from the $SiH_4$–$H_2O_2$ reaction

When the $SiH_4 : H_2O_2$ ratio was reduced to less than about 1 : 4, the spectrum of the film showed an additional peak at 880 $cm^{-1}$. This has been observed in other under-oxidized silica films and has been assigned to the phase $Si_2O_3$.[6] The spectrum obtained by X-ray photoelectron spectroscopy (XPS) of both this under-oxidized film and the standard fully oxidized film showed no difference in the shape or position of the Si 2p peaks. However, both samples were exposed to air before insertion into the spectrometer and this may have caused oxidation of the surface of the under-oxidized film.

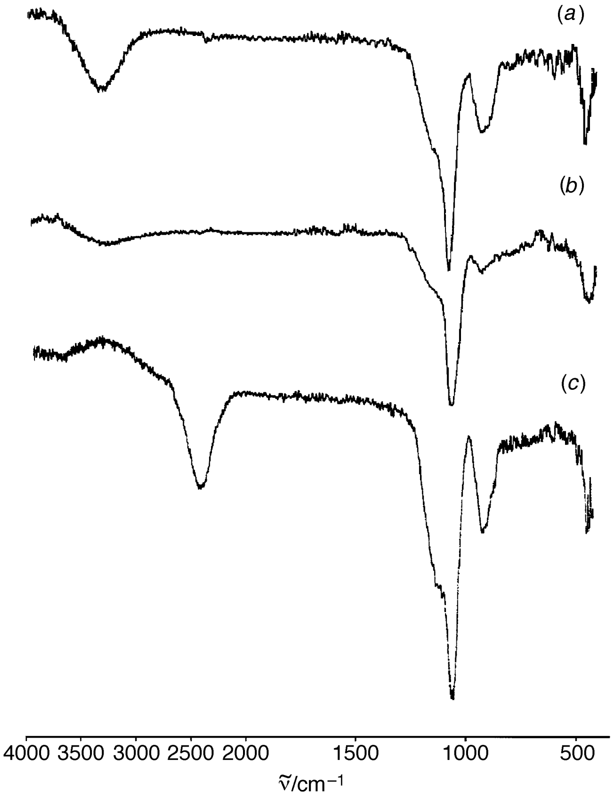

**Fig. 2** Infrared spectra of (*a*) a silica film formed from the $SiH_4$–$H_2O_2$ reaction, (*b*) after treatment of the film with hexamethyldisilazane and (*c*) after treatment of the film with the vapour of $D_2O$

The fully oxidized films underwent rapid exchange with ambient moisture. When a film which gave an infrared spectrum like that in Fig. 2(*a*) was exposed to the vapour of $D_2O$ its infrared spectrum changed quickly to that in Fig. 2(*c*) showing that all of the OH groups had been replaced by OD. Exposing this film to moist air caused re-conversion to the original form. Thus infrared studies of the reactions of $SiD_4$ with excess $H_2O_2$ (containing some $H_2O$) and $SiH_4$ with excess $D_2O_2$ (containing some $D_2O$) gave no useful information about the mechanism of the reaction as the observed form of the infrared spectrum was determined entirely by the $H_2O$ or $D_2O$ present in the ambient vapour. A comparison of the spectra of Fig. 2(*a*) and 2(*c*) showed that both had a peak at 930 $cm^{-1}$ suggesting that this band is primarily associated with an Si–O(E) (E = H or D) stretch such that changing H for D does not noticeably affect its position.

Replacement of $SiH_4$ with $Si_2H_6$, $Si_3H_8$ or $Si_4H_{10}$ in the reaction with excess $H_2O_2$ vapour caused no obvious changes in the form of the deposited silica film indicated by IR and XPS spectra and by physical appearance. If there was insufficient excess of $H_2O_2$ vapour the band at 880 $cm^{-1}$ appeared as with under-oxidized $SiH_4$–$H_2O_2$ mixtures and, with severe under-oxidation, a ν(SiH) band at 2260 $cm^{-1}$ also appeared.

When $SiD_4$ and 70% $H_2O_2$ vapours were reacted in a 1:10 mol ratio, it was found by mass spectrometry that $D_2^+$ and $HD^+$ (but no detectable $H_2^+$) were liberated in a mol ratio of 3:1. Reacting an equimolar mixture of $D_2$ and $SiH_4$ with $H_2O_2$ gave no detectable HD in the effluent gases although $H_2$ was then abundant.

For the reaction of $SiH_4$ with an excess of $H_2O_2$, the amount of $H_2$ released per mol of $SiH_4$ consumed was quantified by measuring both the total $H_2$ evolved and the amount of $SiH_4$ remaining unreacted. The results showed that under the normal conditions used to give flowy silica films with the wafer at *ca.* 5 °C and the reactor walls at 22 °C , 0.72 mol of $H_2$ was produced per mol of $SiH_4$ consumed and about 19% of the $SiH_4$ introduced was unreacted. When the reactor walls and the wafer were cooled to 0 °C, 10% of the $SiH_4$ introduced remained unreacted. Heating the reactor and wafer to *ca.* 100 °C gave 32% of unreacted $SiH_4$. This seemed to indicate that the reaction was occurring either on the reactor surface or by a complex gas-phase process.

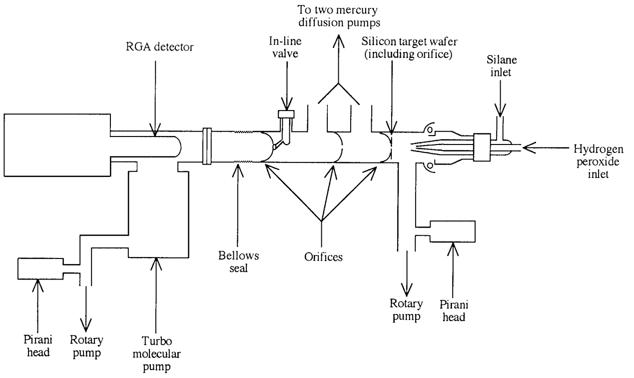

**Fig. 3** Apparatus for investigating the $SiH_4$–$H_2O_2$ reaction by mass spectrometry

Direct evidence of whether the reaction betwen $SiH_4$ and $H_2O_2$ was occurring partly in the gas phase or only in contact with the solid surface was gathered in two ways. First, by mass spectrometry using the apparatus shown in Fig. 3. The $SiH_4$ and $H_2O_2$ vapours were mixed as they left the concentric nozzle under the same pressure conditions as used for the infrared studies. Initially, the gas stream impinged on to a silicon wafer with a small hole in it which allowed part of the gas stream to pass by line-of-sight path to the ion source of the mass spectrometer as shown in Fig. 3. Silica was deposited on the wafer but the mass spectrum showed no peak above *m/z* 34, $H_2O_2^+$, except a peak at *m/z* 44. This peak was also apparent using $H_2O_2$ in the absence of silane and it appears to be due to $CO_2$ dissolved in the $H_2O_2$. The abundance of the peak could be greatly enhanced by bubbling $CO_2$ through the liquid $H_2O_2$ before it was added to the mass spectrometer system. Using a whole range of ratios from an excess of $SiH_4$ to an excess of $H_2O_2$, no higher mass peaks were seen. With an excess of $SiH_4$, *m/z* 30 was dominant and this spectrum changed to give *m/z* 32 as the dominant peak as the $H_2O_2$ concentration was increased.

As the above results gave no evidence for a gas-phase reaction, the target was changed to a platinum gauze. This had no effect on the form of the spectra of the vapour species passing through the gauze although silica was deposited on the gauze. Replacing $SiH_4$ by $Si_2H_6$ gave peaks for $Si_2H_6$ in the range *m/z* 56–62 but no other new peaks in the mass spectrum.

Secondly, the apparatus of Fig. 4 was used to study co-condensation of $Si_2H_6$ and $H_2O_2$ vapour on a liquid nitrogen cooled silicon window by infrared spectroscopy; disilane was chosen because it more readily condensed on the cold window. The apparatus was designed to allow $Si_2H_6$ and $H_2O_2$ to mix under normal deposition conditions (giving a silica film on the horizontally mounted silicon test sample shown in Fig. 4) while a series of pulses of the mixed vapours were extracted for deposition on the liquid nitrogen cooled window. The infrared spectrum of the deposit showed the presence only of $Si_2H_6$, $H_2O_2$ and $H_2O$. No ν(SiO) bands were detected. Raising the temperature of the window to −100 °C allowed the $Si_2H_6$ to be pumped away without reaction. At higher temperatures, all the $H_2O$ and $H_2O_2$ could also be pumped away leaving no residue on the window.

## Plasma activated water reacting with silane

As described in the Experimental section, $D_2O_2$ was made by a modification of a published method[7] in which $D_2O$ vapour at low pressure was subject to a microwave discharge and the resulting radicals were condensed on a liquid nitrogen cooled

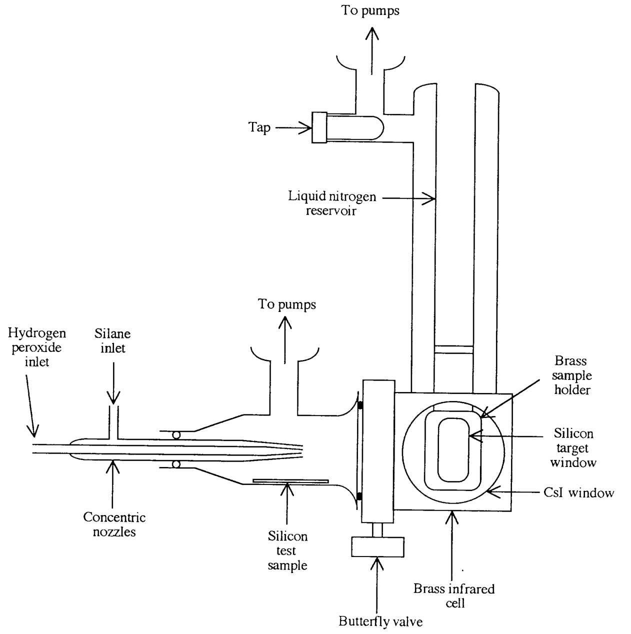

**Fig. 4** Apparatus for sampling from a gas stream containing $SiH_4$ and $H_2O_2$ with a low-temperature infrared gas cell

surface. The formation of $D_2O_2$ by this process appeared to involve the combination of OD radicals on the cold surface while the D atoms were lost as $D_2$. An attempt was then made to see if microwave activated $H_2O$ would behave in the same way as preformed $H_2O_2$ in its reaction with silane.

The reaction was performed in two types of apparatus shown in Fig. 5(*a*) and 5(*b*). The apparatus of Fig. 5(*a*) using about 100 W microwave energy in a tuned cavity around a quartz tube did not produce a sufficient concentration of OH radicals to have any prospect of forming a flowy silica film when the radicals were mixed with $SiH_4$. Thin silica films could be grown over a period of some minutes and there was a tendency for these to show peaks at 880 and 2260 $cm^{-1}$ in their IR spectra, characteristic of under-oxidized products. Much more rapid film growth was possible in the apparatus of Fig. 5(*b*) in which water vapour was activated by passing it through a Pyrex tube within a 750 W domestic microwave oven. The operating pressure and the rate of film growth could be made comparable to those needed to develop flowy films in the reaction of $SiH_4$ with $H_2O_2$. However, although the IR spectra of the microwave-generated films showed them to be identical to those of our earlier films, they were not flowy. The silica deposition followed the contours of the substrate rather than planarizing them. When the $SiH_4$ was mixed with the stream of microwave-activated water vapour, some nucleation of solids was observed in the gas stream directly above the $SiH_4$ inlet. This is in contrast to the $SiH_4$–$H_2O_2$ reaction for which there has been no evidence of nucleation of solids in the gas stream.

## Discussion

Evidence from the effect of temperature on the reaction efficiency, from mass spectrometry and low-temperature infrared spectroscopy suggests that the $SiH_4$–$H_2O_2$ reaction occurs only in the condensed phase on a surface under the pressure and temperature conditions used. There was no evidence of gaseous intermediates with Si–O bonds. This is in contrast to the many reports in the literature on the oxidation of silane to give silica using thermal reactions[8] or plasma reactions[9] with oxidants which indicate that there is initiation in the gas phase followed by deposition of wholly or partially oxidized silicon species.

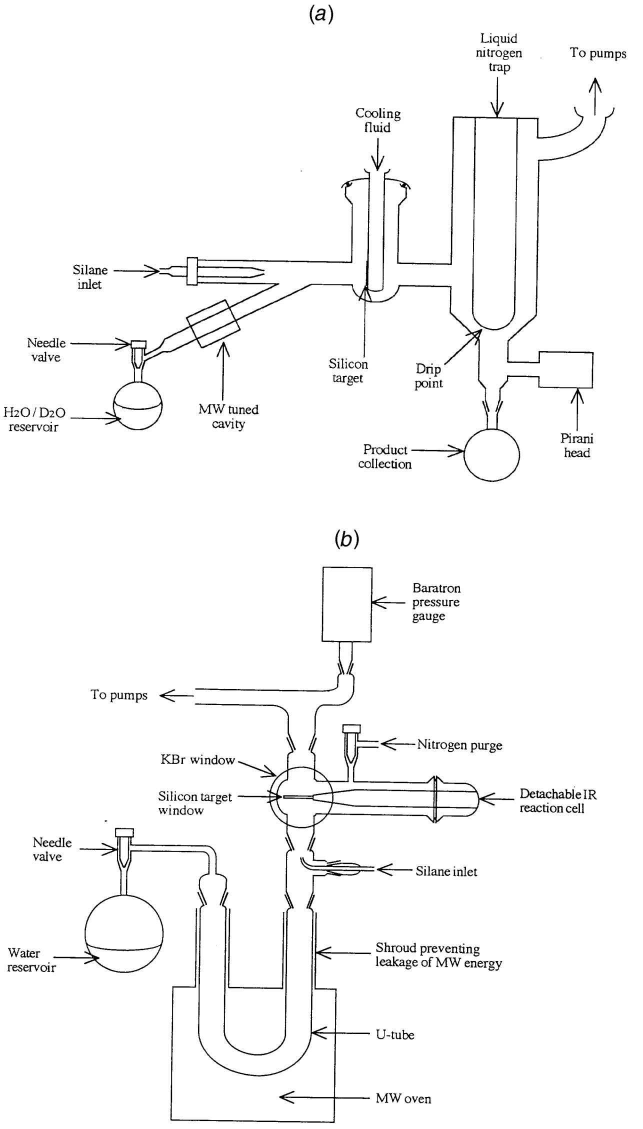

**Fig. 5** (*a*) Microwave plasma apparatus and (*b*) improved microwave plasma apparatus

As only about 36% of the hydrogen theoretically available from $SiH_4$ is observed to be liberated as $H_2$, then the $SiH_4$–$H_2O_2$ reaction occurring on a solid surface cannot follow the simple stoichiometry shown in equation (1). A reasonable explanation

$$SiH_4 + 2H_2O_2 \longrightarrow 2H_2 + [Si(OH)_4] \longrightarrow SiO_2 + 2H_2O \quad (1)$$

of this datum is that the reaction proceeds *via* a free radical mechanism involving $OH^\bullet$, $OOH^\bullet$, $SiH_3^\bullet$ and partially oxidized silyl radicals. These radicals are believed to be prominent in the oxidation of silane in the gas phase.[10,11] An initiation step such as that shown in equation (2) could be followed by reactions

$$SiH_4 + H_2O_2 \longrightarrow H_2SiOH^\bullet + OH^\bullet + H_2 \quad (2)$$

(3)–(5) in which hydrogen from the silane is converted to water

$$SiH_4 + OH^\bullet \longrightarrow SiH_3^\bullet + H_2O \quad (3)$$

$$H_2SiOH^\bullet + H_2O_2 \longrightarrow HSi(OH)_2^\bullet + H_2O \quad (4)$$

$$SiH_3^\bullet + H_2O_2 \longrightarrow H_2SiOH^\bullet + H_2O \quad (5)$$

with no hydrogen evolution. Hydrogen atoms may not be part of the reaction scheme because when the reaction between $SiH_4$ and $H_2O_2$ was carried out in the presence of $D_2$, no HD formation was detected. The majority of evolved $H_2$ came from $SiH_4$

as in the reaction of $SiD_4$ with the normal ten-fold excess of $H_2O_2$, most of the gas released was $D_2$ with less HD and no detectable $H_2$.

The reaction occurred with greater efficiency (in terms of $SiH_4$ usage) as the temperature was lowered to 0 °C. At lower temperatures the residence time of the adsorbed reactant molecules on the surface will increase ( particularly for $H_2O_2$ as it approaches its dew point) and this will help to promote the surface reaction. The solid product that is formed is initially a type of silica gel and its ability to adsorb $SiH_4$ and $H_2O_2$ may promote the reaction. In the case of the higher silanes, oxidation of Si−H and Si−Si must be processes which occur with similar readiness to give the same silica product as from $SiH_4$ and $H_2O_2$. It should be noted that deposition of silica from the $SiH_4$–$H_2O_2$ reaction occurred on various substrates apart from silicon, *e.g.* platinum, copper, silver chloride and the Pyrex reaction vessel, showing that the surface is not chemically involved in the reaction.

The formation of $OH^{\bullet}$ or $OD^{\bullet}$ radicals in a microwave discharge was demonstrated by the successful preparation of $H_2O_2$ or $D_2O_2$ by a modification of a published procedure.[7] Unlike gaseous $H_2O_2$, these gaseous radicals seemed able to attack $SiH_4$ in the gas phase in line with other studies of silane oxidation.[12] However, we have not demonstrated unambiguously that $OH^{\bullet}$ radicals are the only species of importance in the microwave-induced reaction with $SiH_4$. Hydrogen atoms and some charged species are also present in the plasma and these may be carried out of the plasma to help initiate reaction with $SiH_4$ in the gas phase.

These studies provide only limited information about the processes which lead from the ultimate oxidation products of $SiH_4$ to a solid silica film. The unique ability of this reaction to form flowy films may arise from a semi-liquid sol stage as $Si(OH)_4$ loses water. The liquid medium may contain both $H_2O$ and $H_2O_2$ as the latter is higher boiling than water and will be strongly adsorbed on the surface. If the wafer temperature is >10 °C, flowiness is reduced and this may be because too little $H_2O$ and $H_2O_2$ is retained by the film during the critical growth period promoting gelling. The initially formed films can be smeared like a grease but they harden on standing. In commercial practice, after deposition is complete the films are heated under vacuum to encourage water loss and densification.

The most surprising conclusion from this work is that $SiH_4$ and $H_2O_2$ vapours react only on surfaces and with substantially higher reaction efficiency at 0 than at 100 °C. Although the work throws some light on the chemical nature of the condensate, there is much still to be learned about the nature of the flowy material. Studies are continuing on elucidating the chemistry of the reaction by incorporating other vapours with the silane.

## Experimental

### Reagents

The $SiH_4$ used was Argo International electronic grade. Higher silanes were prepared by hydrolysis of magnesium silicide with 10% aqueous HF and separated and purified by vacuum-line distillation. Hydrogen peroxide from several sources and of several concentrations was used successfully, ranging from 30% supplied by BDH or Fisons, up to 90% from Electrotech. Vacuum microwave dissociation of $D_2O$[7] and condensation of the off-gases on a liquid nitrogen cooled surface as shown in Fig. 5(*a*) was used to form $D_2O_2$ (the silane nozzle and silicon wafer insert were not present for this experiment). The vapour of $D_2O$ was bled from a liquid reservoir through a needle valve and passed through a 11 mm outer diameter quartz tube. Around the tube was a tuned cavity from a 200 W EMS Microtron generator operating at 2450 MHz. With an input of $D_2O$ of 0.7 mmol min$^{-1}$ and a pressure in the condensing region around 8 Pa, about 70 W of microwave power was absorbed. A stream of compressed air was used to cool the quartz tube in the discharge region. After a run lasting 1.5 h, the product was obtained by allowing the liquid nitrogen cooled surface to warm up (resulting in a release of permanent gas) and distilling the condensed $D_2O_2$ into a collecting flask. The condensate was then concentrated to yield *ca.* 0.5 cm$^3$ of 30% $D_2O_2$.

### Film deposition equipment

The apparatus of Fig. 1 was connected to a glass vacuum line and vacuum was provided by a mercury diffusion pump backed by a rotary oil pump. There was a liquid nitrogen cooled trap between the system and the pumps. In a run lasting 1.5 min, 0.22 mmol silane was bled in from a gas burette and 2.2 mmol liquid hydrogen peroxide were sucked in from a reservoir through 4 m of 0.15 mm bore Teflon tubing into an aluminium flash evaporator thermostatted at 75 °C. The two vapours mixed as they left the concentric nozzles shown and travelled *ca.* 5 cm before hitting a 0.5 mm thick silicon wafer (Type N cut on the 100 plane) of area *ca.* 2 cm$^2$ cooled by ice–water to <10 °C. The wafer was mounted within an infrared cell. Silica was deposited on the wafer giving a film *ca.* 1.5 μm thick and also on the glassware in its immediate vicinity. The pressure in the deposition region was 60–130 Pa. At the end of a run, the infrared cell was filled with $N_2$ and detached from the pumping line. Then the silicon wafer was rotated to give a line-of-sight path through it and external KBr windows and the infrared spectra were taken using a PE 1600 FT-IR spectrometer.

The silicon wafer could be removed from the cell in air for investigation of the film by optical or scanning electron microscopy or by XPS using a Kratos XSAM 800 spectrometer.

### Apparatus for mass spectrometric studies

Mass spectrometry studies were carried out using a 1–100 mass unit VG Micromass quadrupole spectrometer pumped by a turbomolecular pump shown in Fig. 3. The mass spectrometer was controlled by a personal computer and the accumulated data from 30 200 ms scans were used to give each displayed spectrum. Attached to the spectrometer through a stainless steel bellows was an all-glass differential pumping system with interconnecting aligned orifices. This allowed the pressure to be dropped in three stages through three successive (2, 1 and 1 mm) orifices from the $SiH_4$–$H_2O_2$ mixing zone pressure of *ca.* 100 Pa, to *ca.* $10^{-1}$ Pa in the first mercury diffusion pumped zone, to *ca.* $10^{-4}$ Pa in the second mercury diffusion pumped zone, to $<10^{-5}$ Pa in the mass spectrometer ionisation region. Successive solid $CO_2$ cooled and liquid nitrogen cooled traps between the pumped regions and the mercury diffusion pumps allowed trapping of $H_2O_2$ (but not silane) at −78 °C and trapping of mercury vapour and silane at −196 °C. It was found essential to avoid condensing $H_2O_2$ vapour with Hg vapour as the mixture exploded on warming towards room temperature. A simple sealing device on the glass orifice adjacent to the mass spectrometer allowed the spectrometer to be isolated from the glass system when desired.

Mixing of $SiH_4$ and $H_2O_2$ was carried out as described above with the concentric nozzles mounted *ca.* 5 cm from the surface of a silicon target with a *ca.* 2 mm hole in it aligned with the other orifices. A silica film formed on this target (with successive runs some silica deposition was also seen around the outlet orifice in the first diffusion pumped stage). The silicon target was replaced by a stainless steel disc with a 2 mm hole in it covered with Pt mesh made of 0.15 mm wire with four openings per mm$^2$.

### Reaction of silane and hydrogen peroxide on a liquid nitrogen cooled surface

The apparatus used (Fig. 4) consisted of a brass infrared cell with CsI windows connected through a 25 mm butterfly valve to a glass reactor housing a concentric nozzle system for mixing $SiH_4$ and $H_2O_2$ vapours. In the cell, a silicon wafer was clamped tight on to a brass sample holder (which sealed into the infrared cell *via* a rotatable O-ring 'muff' seal) to ensure good thermal contact between the wafer and the sample holder. The system was arranged so that when the butterfly valve was opened there was a line-of-sight path between the concentric nozzle system and the centre of the silicon wafer. The whole apparatus was evacuated to $<0.5$ Pa, then the cell was isolated from the nozzle area and was filled with $N_2$ gas to a pressure of 1.3 hPa. Silane and hydrogen peroxide were bled into the reactor through the nozzle system and steady-flow conditions were established at a pressure of approximately 1.3 hPa. Silica deposition was observed on a silicon wafer placed in the reactor showing that deposition conditions had been established. The butterfly valve was then opened for a period of approximately 2 s to deposit material on the cooled silicon wafer. The valve was opened and shut for ten 2 s bursts to give the wafer a chance to cool down between periods of trapping material. After deposition, the cell was sealed and removed from the vacuum line, the sample holder and wafer were rotated through 90° and the infrared spectrum of the deposit on the wafer was taken.

### Silica film formation from silane and plasma dissociated water vapour

The apparatus of Fig. 5(*a*) was used as for $D_2O_2$ production but with a silicon wafer attached to a water-cooled glass support and the addition of silane to the discharge decomposed water vapour stream. Water vapour was bled through the needle valve into the quartz tube at a rate of 0.7 mmol $min^{-1}$ and 70–80 W of microwave power was absorbed. Silane was bled in at varying rates up to 0.09 mmol $min^{-1}$. The pressure in the mixing region was *ca*. 8 Pa. Only thin, non-flowy silica deposits could be formed under these conditions and there was a tendency for them to be under-oxidized.

A 750 W domestic microwave oven was modified[13] to allow water vapour to be passed through the microwave region inside a U-tube of 24 mm internal diameter Pyrex tubing as shown in Fig. 5(*b*) at a rate of 1.9 mmol $min^{-1}$ at a pressure of *ca*. 1 hPa. This caused a bright pink discharge and the Pyrex tube heated up rapidly so that the discharge was never run for more than 2 min at a time. The tubing above the discharge region also got warm and some experiments were conducted in which this part was water cooled but this caused no change in the observed reactions with silane. For silica deposition, silane was introduced through the nozzle above the discharge at a rate of 0.14 mmol $min^{-1}$. A faint white smoke was visible where the silane mixed with the dissociated water vapour before the gases impinged on to a silicon wafer. Microscopic investigation of the silica film deposited on a line-etched wafer showed it was not flowy, *i.e.* the silica layer followed the contours of the wafer.

## Acknowledgements

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