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Reaction of hydrogen peroxide with organosilanes under chemical vapour deposition conditions

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When a stream of vapour at low pressure which contained a mixture of H_2O_2 with an organosilane, $RSiH_3$ (R = alkyl or alkenyl), impinged on a silicon wafer, deposition of oxide films of nominal composition $R_xSiO_{(2-0.5x)}$, where $x = \leq 0.17$, was observed. The reactions which accompanied oxide film formation liberated a range of volatile organic compounds consistent with release of $R^\bullet$ radicals in a novel cleavage of Si–C bonds. No oxidation was detected for silanes containing C_3 or higher alkyl groups or C_5 or higher alkenyl groups. Possible mechanisms for the Si–C bond cleavage reaction are discussed, with energetic rearrangement of radical intermediates of type $Si(H)(R)(OOH)^\bullet$ being favoured.

In earlier papers, reactions of hydrogen peroxide vapour at low pressure with pure silane[1] or with silane mixed with other main group hydrides[2] on the surface of silicon wafers were described. The purpose of that work was to try to understand the chemistry of a commercially useful process for forming self-planarising layers of silica as a dielectric on silicon wafers.[3] It was established that the reactions occurred only in the condensed phase and probably proceeded by free radical mechanisms. The self-planarising effect was found to be very sensitive to reaction conditions and the presence of other compounds, but substantial incorporation of other oxides into the silica film was possible.

In this paper the reaction of hydrogen peroxide vapour with a wide range of organosilanes is explored, revealing a novel Si–C bond cleavage process.

Results

All the reactions discussed below were carried out under the following conditions. The vapour of a silane was mixed in a flowing gas stream with a 5–10 fold molar excess of the vapour formed by flash evaporation under vacuum of 60% hydrogen peroxide using the apparatus of Fig. 1. If reaction occurred between the silane and hydrogen peroxide, a solid silica film deposited on a silicon wafer placed directly in the vapour stream (and on other surfaces within the reaction chamber). The best self-planarising films were obtained when the wafer was held at 5 °C, but when planarisation was not being tested the wafer temperature was more conveniently held at 20 °C which reduced the risk of condensation of H_2O_2–H_2O vapour on the wafer. The film thickness increased with the length of time of deposition. Highly adherent, smooth films typically 80 to 300 nm thick were laid down in 0.5–2 min. These films were analysed on the wafer mainly by transmission IR spectroscopy. If deposition was carried out for an extended period of time then much thicker depositions were obtained. These films tended to crack away from the silicon wafer under thermal stress so it was then easy to analyse their composition. Excess of reagents and any volatile reaction products were collected and subsequently separated by low temperature, vacuum distillation techniques.

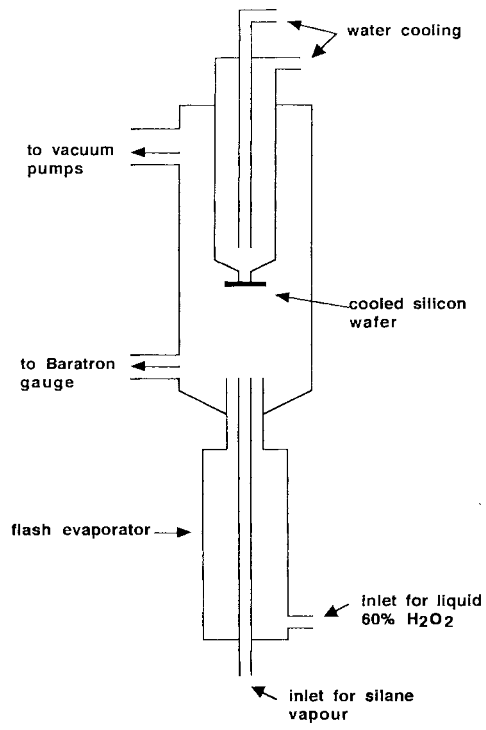

Fig. 1 Apparatus to allow hydrogen peroxide and silane vapours to react on a silicon wafer at low pressure.

Reactions with methylsilane and other alkylsilanes, $RSiH_3$

Methylsilane was found to react easily with H_2O_2 vapour, giving a self-planarising film on the silicon wafer. Optimum film growth occurred at a pressure of reagent vapours of 3–4 hPa, but satisfactory deposition rates were achieved at 1.3 hPa. The IR spectrum of the film (Fig. 2b) was very similar to that of a film formed from treating SiH_4 with H_2O_2 (Fig. 2a). However, there was an additional sharp band at 1284 cm^{-1} (and sometimes a very weak band at 2980 cm^{-1} on the edge of the ν O–H band) showing that Si–CH_3 groups were present. Comparison

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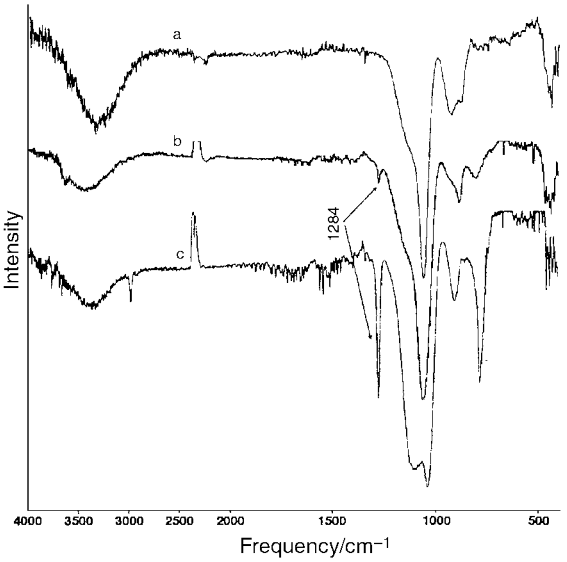

Fig. 2 IR spectra of oxide deposits on a silicon wafer from (a) the SiH_4/H_2O_2 reaction, (b) the CH_3SiH_3/H_2O_2 reaction and (c) the CH_3SiCl_3/H_2O reaction.

of the spectrum of this film with the spectrum of $(CH_3SiO_{1.5})_n$ (Fig. 2c), made by complete hydrolysis of CH_3SiCl_3, showed that the peak at 1284 cm^{-1} was much stronger in the latter spectrum. Chemical analysis of the film from the CH_3SiH_3–H_2O_2 reaction gave a C:Si ratio of *ca.* 1 : 7, confirming that there had been substantial loss of carbon during deposition. Analysis of the vapours from the reaction revealed the presence of CH_4, C_2H_6 and small amounts of $(CH_3SiH_2)_2O$ and $(CH_3SiH_2)_2$ together with unchanged CH_3SiH_3 and H_2O_2.

Neither $(CH_3)_2SiH_2$ nor $(CH_3)_3SiH$ reacted directly with H_2O_2 vapour but an equimolar mixture of $(CH_3)_2SiH_2$ and SiH_4 reacted with H_2O_2 vapour to give a film which had an infrared spectrum identical to that shown for the CH_3SiH_3–H_2O_2 reaction in Fig. 2b. Initially, it was thought that the vapours of $C_2H_5SiH_3$ and H_2O_2 did not react under the conditions used for SiH_4 or CH_3SiH_3 with H_2O_2. However, it was found that the rate of deposition was simply much lower than for the SiH_4 or CH_3SiH_3 systems, and if addition of the $C_2H_5SiH_3$–H_2O_2 reagents was maintained for 5–10 times as long as normally required, adequate film formation would occur. The IR spectrum of this film appeared identical to that shown for the SiH_4–H_2O_2 reaction in Fig. 2a. Ethane and ethene were the main products detected in the off-gases from the reaction but there was also a trace of ethyne and both $(C_2H_5SiH_2)_2$ and $(C_2H_5SiH_2)_2O$ were isolated. The molar ratio of ethene, ethane and ethyne produced was found to be 15 : 6 : 1 respectively, while elemental analysis of the film deposited showed a C:Si ratio of 1 : 4 (*i.e.* one ethyl group to 8 Si atoms).

Using $C_2H_5SiD_3$ in place of $C_2H_5SiH_3$ under the same conditions as above, no formation of a film or of any volatile reaction products was observed indicating that there was effectively no reaction with H_2O_2. There was reaction with H_2O_2 when $C_2D_5SiH_3$ was used in place of $C_2H_5SiH_3$. The off-gases then contained C_2D_5H and C_2D_4.

Various other monoalkylsilanes were tried but none of the higher straight chain or branch chain compounds appeared to react at all with H_2O_2 vapour. Compounds of type $RSiH_3$ which failed to react included all isomers of propyl- and butylsilane, neopentylsilane $[(CH_3)_3CCH_2SiH_3]$, cyclopentylsilane, n-hexylsilane, 1,1,1-trifluoropropylsilane $(CF_3CH_2CH_2SiH_3)$ and trimethylsilylmethylsilane $[(CH_3)_3SiCH_2SiH_3]$.

Efforts were made to promote reaction of several of the above compounds with H_2O_2 by irradiation of the silicon wafer substrate with a collimated beam of light from a 1 kW mercury arc lamp passing through quartz optics, while H_2O_2 vapour and the silane vapour were flowing over the wafer. In no case the reaction occurred to a detectable extent, *i.e.* there was no silica film left on the wafer.

Reactions with alkenylsilanes, $R'SiH_3$

Several silanes with unsaturated organic groups gave silica film formation on reaction with hydrogen peroxide vapour. Vinylsilane was particularly reactive and it readily gave self-planarising films. The IR spectra of a thin film was like that of Fig. 2a but, with a very thick film, weak additional sharp features appeared at 1707 and 1409 cm^{-1}. Chemical analysis of the film indicated a C : Si mole ratio of *ca.* 1 : 5 (*i.e.* one vinyl group to every 10 silicon atoms). Analysis of the off-gases showed the presence of ethene, ethyne and $(C_2H_3Si)_2O$, with the ethene and ethyne being produced in equimolar quantities. Treating $C_2H_3SiD_3$ with H_2O_2 gave C_2H_2, C_2H_4 and C_2H_3D in a mole ratio of *ca.* 1 : 2 : 2.3.

Allylsilane reacted quite readily with H_2O_2 but the reaction occurred most efficiently at a lower wafer temperature than was optimum for methyl- or vinyl-silane. The IR spectrum of a thin film formed from the $C_3H_5SiH_3$–H_2O_2 reaction gave no evidence for the presence of organic groups but chemical analysis of the film showed a C:Si ratio of 1 : 2 (*i.e.* one allyl group for every 6 Si atoms). The off-gases contained two main products, propene and $(C_3H_5SiH_2)_2O$, but also, more surprisingly, some ethene and ethyne. When $C_3H_5SiD_3$ was treated with H_2O_2 the main products obtained were propene and monodeuteriopropene ($CH_2DCH{=}CH_2$). Traces of C_2H_2 and C_2H_4 were also detected as reaction products.

The reactivity of three isomers of $C_4H_7SiH_3$ with H_2O_2 was studied. No deposition was obtained by mixing the vapours of $CH_3CH{=}CHCH_2SiH_3$ or $CH_2{=}CHCH_2CH_2SiH_3$ with H_2O_2 vapour but silica film formation was observed using $H_2C{=}C(CH_3)CH_2SiH_3$ and 2-butene was then detected as a volatile reaction product.

Reactions with substituted methylsilanes, CH_2XSiH_3, and with the disilylalkanes, $CH_2(SiH_3)_2$ and $CH_3CH(SiH_3)_2$

The substituted methylsilanes and disilylalkanes shown in Table 1 all reacted well forming films under standard conditions with hydrogen peroxide but with loss of volatile small molecules.

Reinvestigation of the reaction of H_2O_2 with SiH_4

The observation that volatile products with Si–Si and Si–O–Si bonds were formed when H_2O_2 reacted with alkyl- and alkenylsilanes prompted a fresh study of the reaction of H_2O_2 with SiH_4. Analysis of the volatile products showed that small amounts of Si_2H_6 and $(SiH_3)_2O$ were formed along with the H_2 previously reported.[1]

Discussion

Inspection of Table 1 shows that the volatile organic fragments released in each of the reactions of organosilanes with H_2O_2 are broadly consistent with liberation of an alkyl or alkenyl radical which undergoes subsequent reactions to gain or lose a hydrogen atom. Thus, methyl radicals form methane, ethyl radicals form ethene and ethane, and vinyl radicals form ethyne and ethene. The formation of C_2H_4 and C_2H_3D from $C_2H_3SiD_3$ can be seen as a vinyl radical abstracting H from a Si–H bond (or other hydrogen source) or D from a Si–D bond. The radical must be formed by cleavage of a Si–C bond in a process which occurs rapidly at ambient temperatures. In all cases for which quantitative measurements were made, the oxide film created by reaction of an organosilane with H_2O_2 contained only 10–17% of the carbon originally present in the organosilane. The remaining 83–90% of the combined carbon was lost, mainly as

Table 1 Silanes reactive towards H_2O_2 under the experimental conditions and the volatile products liberated in the reactions

Organosilane investigated	Volatile products detected
Silane (SiH_4)	Disilane, disiloxane
Methylsilane (CH_3SiH_3)	Methane, ethane, 1,2-dimethyldisilane ($[MeH_2Si]_2$), 1,3-dimethyldisiloxane ($[MeH_2Si]_2O$)
Ethylsilane ($C_2H_5SiH_3$)	Ethene, ethane, ethyne, 1,2- diethyldisilane, 1,3-diethyldisiloxane
Vinylsilane ($C_2H_3SiH_3$)	Ethene, ethyne, 1,3-divinyldisiloxane
Allylsilane ($C_3H_5SiH_3$)	Ethene, ethyne, propene, 1,3-diallyldisiloxane
1,2-Disilylethane ($SiH_3[CH_2]_2SiH_3$)	Ethene, ethyne, vinylsilane
2-Methyl-2-propenylsilane ($CH_2C[CH_3]CH_2SiH_3$)	Isobutene ($CH_2C[CH_3]_2$)
Chloromethylsilane ($ClCH_2SiH_3$)	Ethane, ethene, ethyne, chloromethane
1,1-Bis(silyl)ethane ($[SiH_3]_2CHCH_3$)	Silane, ethene, ethyne, ethane
Disilylmethane ($[SiH_3]_2CH_2$)	Ethene, ethane, methylsilane, ethylsilane
Methoxymethylsilane ($CH_3OCH_2SiH_3$)	Dimethyl ether (CH_3OCH_3)
Vinylsilane-*d*₃ ($C_2H_3SiD_3$)	Ethyne, ethene, monodeuterioethene
Ethylsilane-*d*₅ ($C_2D_5SiH_3$)	Ethane-*d*₅ (C_2D_5H), ethene-*d*₄ (C_2D_4)
Allylsilane-*d*₃ ($C_3H_5SiD_3$)	Propene, 3-deuteriopropene (CH_2CHCH_2D), ethene, ethyne

volatile organic compounds as no involatile oxidation products of the organic moieties were detected. This appears to be a novel Si–C bond cleavage reaction. There have been many previous experimental and theoretical studies of the mechanism and kinetics of gas phase radical reactions involved in oxidation of SiH_4[4–7] but apparently no comparable studies on reactions of the organosilanes, $RSiH_3$, which could throw light on the mechanism of the observed Si–C bond cleavage. In addition, earlier studies showed clearly that the reaction between silanes and H_2O_2 occurs on surfaces not in the gas phase,[1] so that any kinetic data for gas phase reactions have to be used with caution when considering a surface reaction. Nevertheless, it seems highly probable that in the surface reactions, as in gas phase oxidations of silanes, free radical reactions predominate.

The hydrogen peroxide vapour formed by flash evaporation very likely contains a low concentration of $HO^\bullet$ which is then available for attacking silane molecules or hydrogen peroxide molecules when the vapours impinge on a surface. Considering direct attack of $HO^\bullet$ on a silane, $RSiH_3$, where R = H, alkyl or alkenyl, four reactions (a)–(d) need to be compared. In some

$$\mathrm{RSiH_3 + HO^\bullet \longrightarrow RSiH_2^\bullet + H_2O} \tag{a}$$

$$\mathrm{\longrightarrow RSiHOH^\bullet + H_2} \tag{b}$$

$$\mathrm{\longrightarrow SiH_3OH + R^\bullet} \tag{c}$$

$$\mathrm{\longrightarrow RSiH_2OH + H^\bullet} \tag{d}$$

mechanistic studies of SiH_4 oxidation at elevated temperatures, reaction (a), which is known to be fast and exothermic, is believed to be an important process.[6,8] In oxidation of SiH_4, reaction (b) is thermodynamically more favorable than (a)[8] and the observation that, in the reaction of SiH_4 and H_2O_2, H_2 is formed provides evidence of a contribution from a reaction such as (b).[1] For the case where $R = CH_3$, (c) is probably slightly more exothermic than (d) but both reactions are less exothermic than (a) or (b).[9] If reaction (c) were important, it would provide a ready explanation for the observed Si–C bond cleavage. However, there is evidence against a significant contribution from reaction (c). A simple silanol such as SiH_3OH would be expected to undergo a rapid condensation reaction to form $(SiH_3)_2O$. However, in every case for which complete product analysis was possible, reactions of $RSiH_3$ compounds with H_2O_2 gave compounds of type $(RSiH_2)_2O$ but no $(SiH_3)_2O$ was detected as a volatile product. This seems to indicate that $RSiH_2OH$ was present in appreciable amounts and that some of it condensed spontaneously to $(RSiH_2)_2O$ but that SiH_3OH was not present. It cannot be concluded from these observations that reaction (d) occurred while (c) did not as $RSiH_2OH$ may have been formed by a different reaction, namely (e).

$$\mathrm{RSiH_2^\bullet + H_2O_2 \longrightarrow RSiH_2OH + HO^\bullet} \tag{e}$$

Dimerisation of $RSiH_2^\bullet$ may have led to the formation of the observed disilane products, $(RSiH_2)_2$. It is known that Si_2H_6 will react like SiH_4 with H_2O_2 to give silica[1] and it is likely that all of the disilanes detected would have been susceptible to further oxidation if they had not escaped as vapours from the surface reaction.

The cleavage of the Si–C bond could have been caused by reactions involving the radical products of reactions (a) and (b). As there was a large excess of H_2O_2 in the surface reactions, it is possible that $RSiH_2^\bullet$ and $RSiH(OH)^\bullet$ reacted with H_2O_2 as in eqns. (f) and (g). The hydroperoxysilicon radicals created would

$$\mathrm{RSiH_2^\bullet + H_2O_2 \longrightarrow RSiH(OOH)^\bullet + H_2} \tag{f}$$

$$\mathrm{RSiH(OH)^\bullet + H_2O_2 \longrightarrow RSi(OH)(OOH)^\bullet + H_2} \tag{g}$$

have been highly unstable and may have decomposed spontaneously and exothermically with elimination of $R^\bullet$ or $H^\bullet$, eqns. (h)–(j). The silicon-containing products from reactions (i)

$$\mathrm{RSiH(OOH)^\bullet \longrightarrow SiH(OH)({=}O) + R^\bullet} \tag{h}$$

$$\mathrm{\longrightarrow SiR(OH)({=}O) + H^\bullet} \tag{i}$$

$$\mathrm{RSi(OH)(OOH)^\bullet \longrightarrow Si(OH)_2({=}O) + R^\bullet} \tag{j}$$

and (j) are fully oxidised and would have condensed to polymeric organosiloxanes and to silica respectively. It must be assumed that reactions (h) and (j) were more significant than (i) to account for the extent of the experimentally observed loss of R groups. Reactions involving the $HOO^\bullet$ radical, formed rapidly from H_2O_2 and $HO^\bullet$,[10,11] could provide alternative pathways to the hydroperoxysilicon radicals shown first in reaction (f) and (g).

Considering now the fate of the H(OH)Si=O reaction product from reaction scheme (h). It would certainly have undergone polymerisation at the silicon–oxygen double bond to give ring and ultimately chain oligomers, $[OSiH(OH)]_n$. In the case of $H_2Si{=}O$, such polymerisation reactions have been calculated as occurring without an activation barrier.[12] Since the final product of the reactions of $RSiH_3$ with H_2O_2 was mainly silica, there must have been further attack on the residual Si–H moiety by $HO^\bullet$ or other radicals leading to oxidation to Si–OH, and condensation of Si–OH groups with elimination of water. The condensation would have resulted in the formation of a silica sol containing small silica particles and oligomers which would have undergone gellation and solidification on drying under high vacuum.

The observation that $C_2H_5SiH_3$ reacts with H_2O_2 vapour, albeit slowly compared to CH_3SiH_3, whereas $C_2H_5SiD_3$ does not react, points to a strong isotope effect. From data reviewed by Atkinson,[13] the rate constant for the $CH_4/HO^\bullet$ reaction is about a factor of ten higher than that for the $CD_4/HO^\bullet$ reaction. If the rate constants for the reactions of $C_2H_5SiH_3$ and

$C_2H_5SiD_3$ with H_2O_2 differ by a similar ratio this could be enough to determine that a radical chain reaction can succeed with $C_2H_5SiH_3$ but not with $C_2H_5SiD_3$. Similar small changes in the constant for the rate determining reaction, caused by different organic substituents, may determine which organosilanes were observed to react and which did not react with H_2O_2.

The isotope effect is not restricted to $C_2H_5SiD_3$ as CH_3SiD_3, $C_2H_3SiD_3$ and $C_3H_5SiD_3$ gases were all significantly less reactive towards H_2O_2 vapour than were their undeuteriated analogues. The nature of R will have had additional effects on the reaction rate through electronic and steric factors. The subtlety of these effects is shown by the result that only $H_2C{=}C(CH_3)CH_2SiH_3$ of the three isomers of $C_4H_7SiH_3$ used showed any reaction with H_2O_2 vapour.

Considering further the data of Table 1, the elimination of chloromethane from $ClCH_2SiH_3$ and of dimethyl ether from $CH_3OCH_2SiH_3$ appears similar to the elimination of methane from CH_3SiH_3 and may have involved the intermediacy of $CH_2Cl^•$ and $CH_3OCH_2^•$ radicals respectively. However, the elimination of some SiH_4 along with C_2H_6, C_2H_4, and C_2H_2 from $CH_3CH(SiH_3)_2$ implies that $SiH_3^•$ as well as organic radicals could have been liberated.

In conclusion, reactions between the vapour of hydrogen peroxide and the vapour of some organosilanes, $RSiH_3$, lead to the formation of oxide films of composition $R_xSiO_{(2-0.5x)}$, where $x \leq 0.17$. In all cases in which the organosilane gave film formation, Si–C bond cleavage also occurred giving rise to volatile organic products apparently derived from liberated organic radicals.

Experimental

Synthesis of organosilanes

Reduction of $RSiCl_3$ compounds. Reduction of commercially available organotrichlorosilanes using lithium aluminium hydride was used to prepare many of the $RSiH_3$ compounds for this work. The $LiAlH_4$ was suspended in tetraglyme (tetraethylene glycol dimethyl ether; 2,5,8,11,14-pentaoxapentadecane). In this way the volatile organosilanes could be produced and vacuum pumped from the reaction vessel with little contamination of or by the the solvent. In setting up the reduction flask, *ca.* 80 cm^3 of dried and degassed tetraglyme were placed in a 3 litre reaction bulb and 8–10 g of $LiAlH_4$ were added slowly under N_2. Once addition of the $LiAlH_4$ was complete, the flask was sealed and pumped on until evolution of gas ceased. The preparation of $MeSiH_3$ is given below as a typical example; many organtrihalogenosilanes were reduced in a similar manner.

The reaction flask was connected to the vacuum line and evacuated. On back filling with nitrogen the rotating side arm was removed and trichloromethylsilane added (4.7 g, 31.4 mmol). The side arm was reconnected and the trichloromethylsilane frozen whilst the flask was brought under vacuum once again. Once evacuation of the flask was complete it was sealed from the vacuum line and the $MeSiCl_3$ allowed to melt. The liquid trichloromethylsilane was then added slowly by gently rotating the side arm to the $LiAlH_4$ suspension which was being stirred. The flask contents were stirred for 10–30 minutes ensuring reduction was complete after which the products were pumped out and condensed in a cold trap. Distillation of the product yielded $MeSiH_3$ (1.3 g, 28.3 mmol, 90%).

The following organosilanes were prepared in a similar fashion: silane, ethylsilane, n-propylsilane, n-butylsilane, n-hexylsilane, vinylsilane, allylsilane, 1,2-disilylethene, chloromethylsilane, cyclopentylsilane and 1,1,1-trifluoropropylsilane.

Purification of the $RSiH_3$ products was simplified as there was no production of the partially reduced compounds ($RSiH_xCl_{3-x}$), and yields were typically high. Often small volumes of silane (SiH_4) were distilled from the flask along with the desired product. This came from the disproportionation of $RSiH_3$, a reaction catalysed by the aluminium chloride ($AlCl_3$) produced during the reduction.[14]

The main advantage of this preparative method was the ability to use the reduction flask numerous times before the $LiAlH_4$ became exhausted, thus saving time and simplifying one of the major synthetic routes in this work.

Grignard synthesis. When trichlorosilanes were not available commercially, suitable precursors to the desired organosilanes were prepared *via* Grignard reagents. Typically the alkylmagnesium halide was prepared and treated with a two molar excess of trichloro- or tetrachloro-silane. In this way the production of the desired monosubstituted product was maximised. The $RSiCl_3$ or $RSiHCl_2$ species produced would then be reduced as described above.

Organosilanes were prepared as follows. (i) Reaction of tetrachlorosilane with organomagnesium chlorides followed by reduction yielded 2-methyl-2-propenylsilane [$CH_2C(CH_3)$-CH_2SiH_3] (43%), isopropylsilane ($[CH_3]_2CHSiH_3$) (16%) and 3-butenylsilane ($CH_2CHCH_2CH_2SiH_3$) (76%). (ii) Reaction of trichlorosilane with organomagnesium chlorides followed by reduction yielded isobutylsilane ($[CH_3]_2CHCH_2SiH_3$) (38%) and trimethylsilylmethylsilane ($[CH_3]_3SiCH_2SiH_3$) (71%); 2-butenylsilane ($CH_3CHCHCH_2SiH_3$) (28%) and neopentylsilane [$(CH_3)_3CCH_2SiH_3$] (19%) were prepared *via* the corresponding organomagnesium bromide and iodide respectively.

Trichlorosilane–tertiary amine combinations. 1,1-Bis(trichlorosilyl)ethane [$(SiCl_3)_2CHCH_3$] and bis(trichlorosilyl)-methane [$(SiCl_3)_2CH_2$] were prepared as previously reported[15] and gave the desired $(SiH_3)_2CHCH_3$ and $(SiH_3)_2CH_2$ on reduction using $LiAlH_4$. Reference to the work by Mironov *et al.*[16] was used to prepare trichloro(methoxymethyl)silane (CH_3-OCH_2SiCl_3), which upon reduction and distillation gave methoxymethylsilane.

The identity of all the synthesized products was checked from published data on their volatility and their NMR and IR spectra.

Deposition procedure

The general procedure for film deposition using CH_3SiH_3 will be described, a similar procedure was used for each organosilane studied. The apparatus in Fig. 1 was connected to a glass vacuum line and vacuum was provided by a mercury diffusion pump backed by a rotary pump. There was a liquid nitrogen cold trap between the system and the pumps. Before addition of reagents, the apparatus was pumped down to $<10^{-3}$ hPa. A 60% aqueous solution of hydrogen peroxide was sucked from a reservoir through 3 m of 0.15 mm bore Teflon tubing at a rate of 87 mg min^{-1} (1.5 mmol min^{-1} of H_2O_2) into the Teflon lined, aluminium flash evaporator thermostatted at 90 °C. Methylsilane gas was then introduced at a rate of 0.3 mmol min^{-1} by a tube running through the flash evaporator. The H_2O_2 and CH_3SiH_3 vapours mixed as they left the evaporator and travelled *ca.* 6 cm before hitting a piece of silicon wafer (Type N, 0.5 mm thick cut on the 100 plane) of area *ca.* 2 cm^2. Formation of a film on the wafer was easily observed through the glass of the vacuum system and the reaction was continued for 3 min to give a deposited film *ca.* 200 nm thick. The pressure in the deposition region was *ca.* 1.3 hPa as measured by a Baratron gauge. At the end of a run the deposition chamber was re-evacuated to $<10^{-3}$ hPa, after which nitrogen was added and the wafer removed and examined using a PE 1600 FT-IR spectrometer. Thick depositions were obtained by using extended reaction times up to 30 min. These films were removed from the wafer by heating them to *ca.* 80 °C for a few minutes whereupon the film would expand, crack due to stress and peel off.

Characterisation of volatile reaction products

Volatile reaction products were collected by placing a removable, liquid nitrogen cooled trap between the deposition chamber and vacuum line. Separation of the volatile products was achieved under vacuum using a very efficient distillation column,[17] operating over the temperature range −150° to −40 °C, with a Pirani gauge to indicate when a fraction was leaving the column. Products were identified by careful comparison of their gas phase infrared spectra with spectra of authentic samples of the same compound or, in a few cases, with published gas phase spectra.

CAUTION: mixtures of vapours of unchanged silanes and hydrogen peroxide were routinely condensed in a liquid nitrogen cooled trap which was part of the vacuum pump system connected to the apparatus of Fig. 1. It was found that the system could safely be closed down by removing the liquid nitrogen and passing a stream of nitrogen through the trap as it warmed up. The volatile silanes evaporated away from the hydrogen peroxide and were vented to the fumehood duct. An explosion occurred on only one occasion when the nitrogen flow was stopped too soon and the trap subsequently warmed to room temperature.

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