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Formation of oxide thin films from reactions of hydrogen peroxide vapour with gas mixtures containing silane and other hydrides

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When hydrogen peroxide vapour and silane are mixed appropriately at low pressure a self-planarising layer of silica is formed by a surface phase reaction. The effect on the reaction of replacing part of the SiH_4 with GeH_4, PH_3 and B_2H_6 has now been studied. Using GeH_4–SiH_4 mixtures containing up to 27% GeH_4, self-planarising, Ge–Si–O films, rich in germanium were obtained. Films formed by oxidising the same GeH_4–SiH_4 mixtures with plasma cracked water vapour were not self-planarising and contained much less germanium. The mixed oxide films from reacting PH_3–SiH_4 or B_2H_6–SiH_4 mixtures with H_2O_2 vapour were also not self-planarising but were spectroscopically similar to known phosphosilicate or borosilicate glasses.

Some features of the reaction between hydrogen peroxide vapour and silane which can give commercially important planarised silica films have been described in an earlier paper.[1] The reaction was shown to occur not in the gas phase but only on surfaces under conditions which gave the best 'flowy' silica films that are self-planarising and mask line etchings and other surface features. This paper describes work to extend the scope of this chemical vapour deposition chemistry to determine if mixed oxide films, with potential uses as dielectric layers in semiconductor devices, can be produced under the same mild conditions by replacing pure silane by mixtures of silane with various gaseous hydrides.

Results

Optimum conditions for forming flowy silica films arise when a mixture of hydrogen peroxide vapour and silane in a mole ratio of about 10:1 at a pressure of about 1 hPa is passed over a silicon wafer. Reaction also occurs at pressures as low as 0.1 hPa and at all practicable higher pressures to give silica films but the flowy quality of the films is adversely affected.[1]

Reaction of hydrogen peroxide with germane and silane mixtures

No oxide film formation was observed when germane was used in place of silane in mixtures with hydrogen peroxide vapour. Mixtures of GeH_4 with a substantial excess of SiH_4 were more successful and reaction occurred at *ca.* 1 hPa to give flowy films until the GeH_4:SiH_4 mole ratio fell below 1 : 2.7 (27% GeH_4) when no film was deposited. The resulting films were studied by IR and X-ray photoelectron spectroscopy (XPS). Both techniques indicated that the films contained GeO_2 and SiO_2 but it was clear from the Ge:Si mole ratio that the GeH_4 was oxidised preferentially to SiH_4 (see Table 1). This occurred to such an extent that with a mole ratio GeH_4 : SiH_4 of 1 : 3.5 (22% GeH_4 in SiH_4), XPS data indicated that the surface 2-3 nm of the deposited film contained a Ge : Si mole ratio of 4.8 : 1. Characteristic of GeO_2–SiO_2 mixed glasses,[2] the IR spectra of these films changed rather little in overall appearance from those of silica films except in the peak maximum and width of the intense band combining Si—O and Ge—O stretches at 1080 cm^{-1} (high Si) to 1000 cm^{-1} (high Ge). As the mole ratio of germanium increased, the deposited films lost the transparency which is typical of films formed from the SiH_4–H_2O_2 reaction.

Table 1 IR band positions and elemental composition for the oxide films formed from reacting silane + germane with hydrogen peroxide

%GeH_4 in silane	ν(Si—O—Ge)/ cm^{-1}	ν(Si—O—H)/ cm^{-1}	Si : Ge atomic ratio (XPS)
0.5	1076	915	1 : 0.13
2.6	1076	925	1 : 0.77
4.5	1078	928	1 : 1.25
10.0	1078, 1011	930	1 : 2.7
22.0	1080(sh), 1012	930 (sh)	1 : 4.8

Hydroxyl radicals, formed by passing a stream of water vapour through a microwave discharge, reacted in a somewhat different way from H_2O_2 with GeH_4 or with GeH_4–SiH_4 mixtures. First, as reported earlier for the reaction of SiH_4 with microwave cracked water,[1] there was clear evidence of reaction occurring in the gas phase not just on a solid surface. Secondly, the films were non-flowy and the extent of germanium incorporation in the films was substantially less than in the reaction of H_2O_2 with GeH_4–SiH_4 mixtures, *e.g.* a film formed by reacting plasma cracked water with a GeH_4–SiH_4 mixture in a 4 : 1 mole ratio contained the same Ge—Si ratio as a film formed from reaction of H_2O_2 vapour with a GeH_4–SiH_4 mixture in a 1 : 4 mole ratio. Thirdly, a reaction occurred even with pure GeH_4 giving GeO_2 films plus some elemental germanium if there was insufficient excess of $OH^{\bullet}$.

Reaction of hydrogen peroxide with diborane and silane mixtures

Mixtures of diborane with silane up to a limiting B_2H_6 : SiH_4 mole ratio of about 3 : 1 reacted with hydrogen peroxide under the same conditions as with neat silane. However, the films formed were not flowy and they showed a white translucence at higher diborane concentrations. The IR spectra of the films showed progressive growth of a B—O band with increasing concentrations of B_2H_6 in silane. The band appeared initially at *ca.* 1370 cm^{-1} at low B_2H_6 concentrations but moved to lower wavenumber with higher intensity as the concentration of B_2H_6 increased. Fig. 1 shows the spectrum obtained from reaction with hydrogen peroxide vapour with an equimolar mixture of B_2H_6 and SiH_4. The spectrum shows a B—O stretch at 1366 cm^{-1} and a B—O bend at 668 cm^{-1} and the intensities of the main bands are very similar to those of Pyrex glass. There is no evidence that there was any boric acid present as this has a strong B—O stretch at 1194 cm^{-1} not

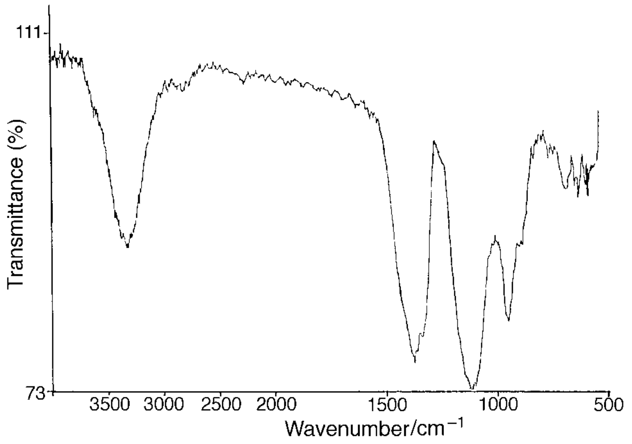

Fig. 1 IR spectrum of an oxide film formed by reaction of an equimolar mixture of B_2H_6 and SiH_4 with H_2O_2 on a silicon wafer

seen in this spectrum or in the spectra of any of the films formed from the B_2H_6–SiH_4–H_2O_2 reaction, although the ν(OH) band at 3400 cm^{-1} is more intense than the equivalent band in the spectrum of an oxide layer formed from the SiH_4–H_2O_2 reaction. [1] The mole ratio of B : Si in Pyrex glass is about 1 : 3.6. This indicates that there was much less boron than silicon in the film shown in Fig. 1, although the hydride mixture used to form the film had a B : Si mole ratio of 2 : 1.

Reaction of hydrogen peroxide with phosphine and silane mixtures

Mixtures of PH_3 with SiH_4 in a mole ratio up to 1 : 4 reacted with hydrogen peroxide vapour to give non-flowy films; at higher PH_3 concentrations no film was formed. The IR spectra of the films showed subtle changes as the relative amount of PH_3 was increased consistent with development of phosphosilicate–silica mixtures.[3] The spectra were difficult to interpret quantitatively because of the overlap of Si—O and P—O bands so the relative amounts of silicon and phosphorus were determined using XPS. As the gas phase concentration of PH_3 increased, there was a roughly linear increase in the P : Si mole ratio in the films from 1 : 0.1 at a PH_3 : SiH_4 mole ratio of 1 : 20, up to a maximum of 1 : 1.35 at a PH_3 : SiH_4 mole ratio of 1 : 4. Even with the most phosphorus rich films, the intensity of the ν(OH) band at 3400 cm^{-1} was only slightly greater than from films obtained by the SiH_4–H_2O_2 reaction using the same post-deposition conditions.

Discussion

Considering the reaction of GeH_4–SiH_4 mixtures with H_2O_2, there was a striking enrichment in germanium in the oxide film relative to the GeH_4 : SiH_4 ratio in the gas mixture which was used. The reaction of silane with hydrogen peroxide is believed to proceed by a free radical process on the wafer surface.[1] These results with GeH_4–SiH_4 mixtures suggest that GeH_4 is playing a very active role in the radical process on the surface. The initiation process may be the same as proposed for the SiH_4–H_2O_2 system[1] in the absence of germane [eqn. (1)]

$$SiH_4 + H_2O_2 \rightarrow H_2SiOH^{\bullet} + OH^{\bullet} + H_2 \qquad (1)$$

but both the $H_2SiOH^{\bullet}$ and $OH^{\bullet}$ formed may react rapidly with GeH_4 giving $GeH_3^{\bullet}$ because the Ge—H bond is relatively weak. The $GeH_3^{\bullet}$ could go on to react with H_2O_2 giving H_2O and $H_2GeOH^{\bullet}$ which would propagate the radical chain as it is further oxidised in stages by H_2O_2 to $Ge(OH)_4$ or its dehydration products. The mechanism of this reaction was not the same as that of the gas phase oxidation of GeH_4–SiH_4 mixtures with plasma cracked water as there was much less germanium incorporation in the film from this latter reaction.

From reactions involving B_2H_6–SiH_4 mixtures and H_2O_2, boron was not enriched in the oxide film relative to its proportion in the gas phase. As there was no evidence from the IR of the oxide film for the formation of boric acid, it is likely that B_2H_6 was attacked most strongly by $H_2SiOH^{\bullet}$ and $HSi(OH)_2^{\bullet}$ radicals perhaps *via* oxygen to boron coordination. There would have been subsequent elimination of H_2 and formation of new radicals containing Si—O—B bonds which yielded ultimately a true mixed oxide. This mixed oxide is formed despite the large amount of water available on the surface to hydrolyse Si—O—B bonds and promote B—OH bond formation.

Commercial applications of oxide films formed from these hydride–hydrogen peroxide reactions depend in part on their flowiness, *i.e.* their ability to self-planarise. Flowiness was observed from mixtures of SiH_4 with GeH_4 but not from mixtures of SiH_4 with B_2H_6 or PH_3. It would seem that replacement of Si—O—Si by Si—O—Ge does not create changes in the developing oxide film which strongly affect the speed of its transformation from a flowy sol to a fixed gel state, whereas, replacement of Si—O—Si by Si—O—B or Si—O—P enhances the change from sol to gel by creating sites where coordinative unsaturation or charge imbalances can help bring particles together.[4]

The reaction with H_2O_2 vapour stopped as the proportion of other hydrides added to SiH_4 was increased to a critical level and no oxide film was formed. Inhibition of the reaction was observed at roughly similar concentrations for GeH_4 and PH_3 (30 and 20% respectively) but at a higher concentration for B_2H_6 (75%). These concentrations do not correlate with the extent of incorporation of the elements with silicon in the oxide film, for which the order is $Ge \gg P > B$. This suggests that there is a very complex balance between radical chain propagation and termination processes in these surface reactions.

In conclusion, the present work shows that the scope of the SiH_4/H_2O_2 reaction can be extended to give mixed oxide films previously only obtainable using more vigorous thermal or electrical discharge oxidation. The films from the GeH_4–SiH_4–H_2O_2 reaction have the additional advantage of being self-planarising, a property seldom appearing in oxide films formed by other methods. There are clearly opportunities to extend this work to give ternary or even more complex mixed oxide systems using mixtures of different hydrides with silane. The practical potential of these films depends not just on composition but also on properties such as their thermal stability and their dielectric characteristics which are currently under investigation.

Experimental

Standard synthetic routes from convenient precursors were used to prepare diborane and germane, whereas silane and phosphine were available as commercial high purity forms. The hydrogen peroxide used (supplied by Electrotech Ltd.) initially contained 70 g H_2O_2 per 100 g of the solution. The vapour formed on flash evaporating this liquid thus contained a H_2O_2:H_2O mole ratio of *ca.* 5 : 4 and when hydrogen peroxide vapour was mixed with a gaseous hydride in a 10 : 1 mole ratio, the true composition of the gas mixture was in the ratio H_2O_2 : H_2O: hydride of 10 : 8 : 1. The reactions with hydrides were not very sensitive to the concentration of H_2O_2 used but with solutions containing <40 g H_2O_2 per 100 g of solution, peaks would appear in the IR spectrum of the oxide films indicating partially oxidised hydride species.

The apparatus used to mix the vapour of hydrogen peroxide with gaseous silane (or silane plus an additive gas or vapour) at a pressure in the range 0.6–5 hPa, so that the vapours could react on the surface of a 10 × 20 mm piece of silicon wafer cooled to 5 °C, has been described elsewhere.[1] Mixtures of silane with the vapours of additives were prepared by standard vacuum line techniques and the gas mixtures were bled into the reaction chamber from a gas burette through a needle valve.

After pumping away adsorbed reagents and water under vacuum (*ca.* 1 Pa) at room temperature for about 1 h, the IR spectra of deposited films were taken in transmission mode using a PE 1600 FT-IR spectrometer.

The oxide coated wafers were removed from the reaction chamber and handled in air before being studied by optical and scanning electron microscopy to find if the oxide films were flowy, *i.e.* forming a planarized layer covering surface features of the wafer. Scanning electron microscopy showed the thickness of films prepared was typically 100–200 nm. In all cases, the dried films appeared crack-free and adhered strongly to the silicon wafer like the films from the SiH_4–H_2O_2 reaction.

Analysis of the oxide film by XPS was also carried out on samples exposed to air. The XPS spectra were obtained with a Kratos XSAM 800 spectrometer using unchromatised Al-Kα radiation (1486.6 eV) with the anode operated at 300 W (15 kV, 20 mA). The spectrometer was operated in the fixed analyser transmission mode with a pass energy of 20 eV. The slit and lens of the spectrometer were set such that the Ag $3d_{5/2}$ peak had an FWHM height of 1.02 eV at this pass energy. Calibration of the energy scale was achieved using the binding energy of the Ag $3d_{5/2}$ peak at 368.2 eV and the Fermi level from pure nickel foil. The piece of silicon wafer on which an oxide film had been deposited was attached to a sample stub covered with copper based adhesive tape. Sample charging was countered by setting the signal from 'adventitious' carbon at 285.0 eV binding energy. Use of the spectra to obtain approximate elemental surface composition of the deposited oxide film was achieved by fitting a Shirley background[5] to the metal $2p_{3/2}$ or $3d_{5/2}$ photoelectron peaks plus the O 1 s peak and measuring the resulting peak area. The peak areas were used in conjunction with the sensitivity factors of Wagner *et al.*[6] to obtain the approximate surface composition of the samples in terms of the relative atomic percent. Peak positions for the different oxide films analysed were as follows: film from SiH_4–GeH_4–H_2O_2; Si 2p, 103.2 eV (lit. for SiO_2 103.3 eV [7]); Ge $2p_{3/2}$, 1221.3 eV (lit. for GeO_2 1220.4 eV [8]). Film from SiH_4–PH_3–H_2O_2: Si 2p, 104.1; P 2p 134.9 eV (lit. for P_4O_{10} 135.3 eV [7]).

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