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Glass-Ceramics for use in Silicon Semiconductor Applications

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Electronic engineers are interested in glass-ceramics for coating and bonding silicon semiconductor material for the fabrication of integrated circuit devices. The glass-ceramics must be able to withstand temperatures of 1100 to 1200° C and should be reasonably well matched in expansion to silicon. Glass-ceramics of the ZnO–Al_2O_3–SiO_2 type, with the addition of various oxides have been examined. It has been shown that additions of CaO, BaO or B_2O_3 give materials which are matched in linear thermal expansion characteristics to silicon, and these materials can be applied to pre-oxidised silicon at temperatures in the region of 1200° C to give smooth, adherent coatings on the silicon, the coatings being refractory at temperatures in excess of 1100° C. The glass-ceramics can also be used to bond together silicon pieces using similar firing schedules to those used to provide the coatings on silicon. By suitable choice of the firing conditions and control of the thickness of the silicon dioxide interlayer, the attack by the glass-ceramic on the underlying silicon can be reduced to a negligible amount. The glass-ceramics of the types examined have been shown to have high volume resistivities (greater than 10^8 ohm cm at 500° C), and can resist the environmental conditions likely to be encountered in diffusion processes.

1. Introduction

A great deal of effort is being applied in research in the field of micro-miniature solid state electronics. Problems exist in the preparation of certain types of circuits, particularly complementary pair circuits, in which two pieces of silicon (*n*-type and *p*-type respectively) have to be arranged together in a predetermined geometrical relationship. In order to do this an insulating material is required which can be used to bond together the pieces of silicon (fig. 1) and also where necessary provide an insulating coating over the resultant unit.

It is essential that the insulating material should wet and adhere strictly to the silicon and also that it should be sufficiently refractory to withstand subsequent processing conditions applied to the silicon. Conventional ceramic materials, whilst they would be sufficiently refractory, would not wet and adhere as required. Glasses could be prepared which would wet and adhere but these would not be sufficiently refractory for the required purpose.

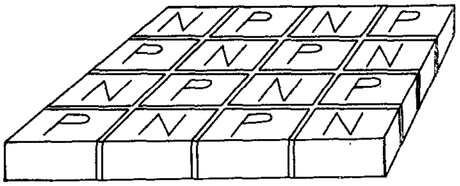

Figure 1 Bonded assembly of *p*-type and *n*-type silicon.

It was considered, however, that a glass-ceramic material might be suitable for this application. Materials of this type have been prepared which can wet and adhere strongly to various substrates and which are also sufficiently refractory for the required application.

The requirements for the glass-ceramic can be set out as follows:

(*a*) The linear thermal expansion characteristics of the glass-ceramic should be similar to those of silicon to ensure that the silicon is not strained or damaged by the coating, and also to ensure satisfactory adhesion to the silicon. The linear thermal expansion coefficient of silicon is in the range 32 to 39 × 10^{-7} per ° C (20 to 500° C), depending on crystallographic direction [1, 2] and it is thought that the linear thermal expansion coefficient of the glass-ceramic should not differ by more than 5 × 10^{-7} per ° C from this and should preferably be lower than that of the silicon. This requirement that the silicon should not be strained is important in connection with semiconductor technology, since excessive dislocations and slip, caused in the silicon by the coating, would render the silicon unsuitable for use as a semiconductor.

(*b*) The glass-ceramic must be able to withstand temperatures up to about 1000 to 1200° C without significant deformation occurring. Temperatures in this region are used in the diffusion processes employed to implant devices in the silicon.

(*c*) The glass-ceramic must be resistant to chemical attack during diffusion processes.

(*d*) The glass-ceramic must be capable of being applied satisfactorily to silicon and be capable of bonding pieces of silicon firmly together at a temperature substantially below the melting point of silicon, which is 1410° C. This requirement may be even more stringent if an intermediate oxide layer of silica is provided between the glass-ceramic and the silicon, since the oxide tends to be unstable and devitrify at temperatures above about 1300° C, and certainly above 1350° C [3].

(*e*) The glass-ceramic should have a reasonably high strength, sufficient to prevent failure during processing and subsequent operating procedures.

(*f*) The glass-ceramic should have a high volume resistivity.

2. Selection of the Glass-ceramic

The glass-ceramic selected must clearly fulfil the above requirements but in addition there are certain limitations on the chemical composition of the material. It must not contain any ions, in particular alkali ions (e.g. Li^+, Na^+, and K^+), which could easily diffuse into the silicon during application and subsequent processing, since this would clearly influence the devices implanted in the silicon. In connection with this, an interlayer of silicon dioxide would act as a barrier to the diffusion of the majority of ions (excepting alkali ions) which could be present in the glass-ceramic.

In previous work carried out in the Nelson Research Centre, investigation of new types of glass-ceramics led to the study of alkali-free alumino-silicate type materials. These possessed moderately low linear thermal expansion coefficients in the range 30 to 70 × 10^{-7} per °C (20 to 500°C) and in addition could be refractory at temperatures in the region of 1200°C. It was within this field of compositions that it was considered glass-ceramics could be obtained which might be suitable for the coating and bonding of silicon. In particular, glass-ceramics of the zinc alumino-silicate type appeared to be suitable for the required application.

Glass-ceramics were prepared of the ZnO–Al_2O_3–SiO_2 type to which additions of other oxides, such as MgO, CaO, BaO, B_2O_3 and GeO_2, were made as given in table I. The glasses were melted in crucibles of high alumina content at temperatures in the range 1400 to 1500° C. After refining to give clear, homogeneous glasses, they were normally cast into cold water to form "frit" (pulverised glass). After drying at 110° C, the glass frits were reduced to powder by milling with flint pebbles, the powder being sufficiently fine to pass through a 200 BS mesh sieve.

It was obviously important to know the linear thermal expansion characteristics of the glass-ceramic coatings on the silicon. The coating is subjected to a fusion process in which the individual powder particles fuse together to form a continuous layer and devitrification occurs during this process. It was considered that it would not be possible to reproduce this on bulk glass since the deformation occurring during this process on these bulk glasses would render the preparation of suitable test samples difficult, and in addition it was realised (on the basis of previous experience) that the crystallisation processes in bulk material might not be the same as in the coatings which originate from powder material. This difficulty was overcome by preparing pressed compacts in the glass powders. Each compact was fired to a temperature at which it first started to deform (i.e. the corners rounded off). This temperature was maintained for up to 15 min to fuse the compact to a non-porous material and also to complete devitrification of the glass. The above process simulated fairly closely the firing of the coatings on to silicon. The compact fusion temperatures for the various materials are given in table I.

The linear thermal expansion characteristics of the fired compacts were then determined in a standard manner using a recording dilatometer. The thermal expansion coefficients, 20 to 500° C, of the various glass-ceramics determined on fused compact samples are given in table I.

TABLE I Properties of the glass-ceramics and their estimated suitability for coating and bonding silicon.

Glass-ceramic ref. no.	ZnO/SiO_2 ratio	Wt % addition	Compact fusion temp. °C	Linear thermal expansion coeff. × 10^7 20–500° C	Volume resistivity at 500° C ohm cm	Firing temp. on silicon ° C	Suitability for coating silicon based on expansion characteristics
1	1.08	—	1320	90.6	—	—	No
2	1.43	10% B_2O_3	—	40.8	—	1080	Yes
3	1.70	15% B_2O_3	—	44.3	—	—	No
4	1.11	1% CaO	1320	84.1	—	—	No
5	0.96	5% MgO	1280	76.6	—	—	No
6	0.84	10% MgO	1280	91.1	—	—	No
7	0.72	15% MgO	1260	103.0	—	—	No
8	0.96	5% CaO	1220	67.4	—	—	No
9	0.84	10% CaO	1220	31.5	—	1170	Yes
10	0.72	15% CaO	1200	38.5	—	1140	Yes
11	0.60	20% CaO	1160	43.2	—	—	No
12	1.03	4% BaO	1280	66.1	—	—	No
13	0.95	10% BaO	1240	32.5	5.4 × 10^8	1230	Yes
14	0.76	—	1320	112.1	—	—	No
15	0.96	—	1320	88.0	—	—	No
16	1.35	—	1320	60.4	—	—	No
17	1.50	30% B_2O_3	—	41.1	—	—	No
18	0.75	10% B_2O_3	1220	43.4	—	1220	Yes
19	1.18	10% B_2O_3	—	36.6	1.3 × 10^8	1180	Yes
20	1.17	15% B_2O_3	—	31.7	—	1180	Yes
21	1.33	16% B_2O_3	—	36.9	6.3 × 10^8	1170	Yes
22	0.82	7% B_2O_3	1280	41.6	—	1260	Yes
23	0.88	5% B_2O_3	1320	33.2	—	1260	Yes
24	0.75	10% GeO_2	> 1360	101.6	—	—	No
25	1.43	10% GeO_2	1320	63.5	—	—	No
26	0.96	5% BaO_2	1300	48.4	—	—	No
27	0.84	10% BaO	1260	41.3	—	1240	Yes
28	0.72	15% BaO	1240	38.7	—	1200	Yes
29	0.60	20% BaO	1280	37.7	—	1220	Yes
30	1.55	5% BaO	1300	29.2	1.4 × 10^8	1300	Yes
31	1.22	5% BaO	1310	36.4	—	1280	Yes
32	1.70	—	1320	67.4	—	—	No

It was clear from the expansion characteristics of the various glass-ceramics tested, that the base $ZnO–Al_2O_3–SiO_2$ materials and those containing MgO and GeO_2 were not suitable for the present application in view of the relatively high linear thermal expansions of these materials. Also the linear thermal expansion characteristics of these glass-ceramics showed a marked inflection at temperatures in the region of 250 to 350° C indicating the presence of cristobalite as one of their crystal phases (this has been confirmed by X-ray diffraction analysis). In addition it was found that the presence of MgO leads to the formation of a high expansion magnesium silicate phase (Mg_2SiO_4: forsterite), and consequently when MgO is present it is not possible to obtain a good thermal expansion match to silicon. Examples of the linear thermal expansion characteristics of these unsatisfactory materials are shown in fig. 2.

Only those glass-ceramics can be considered which do not contain substantial proportions of high expansion crystal phases and in which the formation of crystal phases such as cristobalite, which exhibit large volume changes on phase inversion, is inhibited. In the $ZnO–Al_2O_3–SiO_2$ type of glass-ceramics studied in the work described in the present paper, these requirements can be met by the inclusion of B_2O_3, BaO or CaO in the compositions given in table I. Examples of the linear thermal expansion characteristics of glass-ceramics matched in expansion to silicon are shown in fig. 3.

Generally the glass-ceramics suitable for

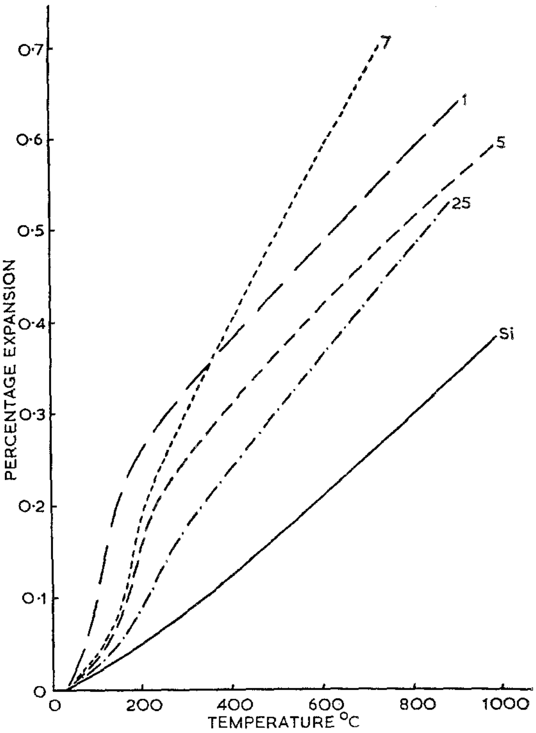

Figure 2 Linear thermal expansion characteristics of glass-ceramics Nos. 1, 5, 7, 25 fired to compact fusion temperatures.

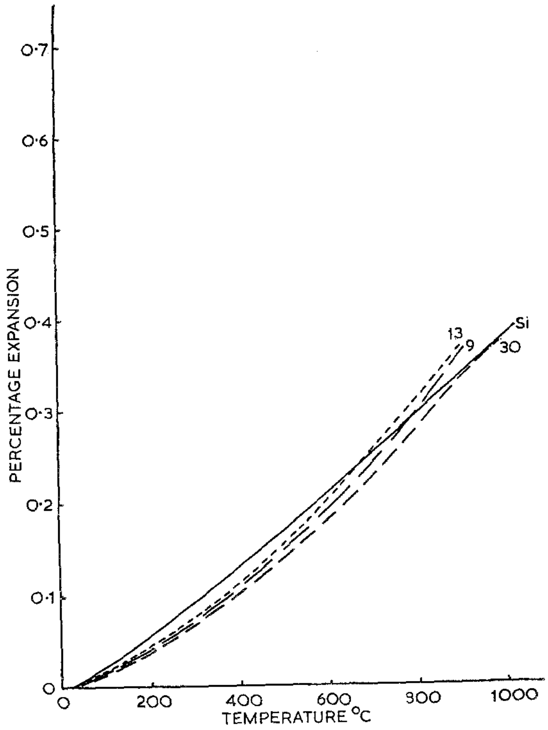

Figure 3 Linear thermal expansion characteristics of glass-ceramics Nos. 9, 13, 30 fired to compact fusion temperatures.

application to silicon contain major proportions of zinc orthosilicate (Zn_2SiO_4) and zinc aluminate ($ZnAl_2O_4$) as shown by X-ray diffraction analysis.

Other properties of these suitable glass-ceramics have been determined. They have been shown to have high volume resistivities, and at a temperature of 500° C have resistivities in excess of 10^8 ohm cm. Typical values are given in table I. They also have high resistances to the environmental conditions which occur during diffusion processes in the fabrication of silicon semiconductor devices. For example, Glass-ceramic No. 18 fired to a temperature of 1080° C for a period of 16 h in an atmosphere of dried hydrogen chloride gas lost only 0.29% of its original weight. The surface of the sample lost some of its original lustre but no deformation occurred.

3. Application of the Glass-ceramics to Silicon

In order to facilitate the work on application of these coatings it was considered to be worthwhile to obtain some idea of the fusion temperatures of the glass-ceramics onto silicon before carrying out coating trials. Two techniques were employed as follows:

(*a*) The measurement of contact angle has been advantageously used in the past to determine the temperature at which a particular glass starts to wet a substrate and it was thought that it would be of value in the present work. Cube samples, approximately $\frac{1}{8}$ in. side, of the glasses listed in table I, were placed on preoxidised silicon slices in the centre of a tube furnace. An atmosphere of dried, high purity argon was passed into the tube. The glass cubes on the silicon were viewed using a telescope fitted with fixed and movable scales graduated in degrees. The temperature was raised at a rate of approximately 3° C/min. The sequence of changes observed in the interior angle of contact in the glass sample against the silicon as the temperature was raised is shown in fig. 4. The temperature at which the contact angle fell below 90° was determined.

(*b*) A second method, which it was thought would be more accurate than the measurement of contact angle, was to use the powder compact

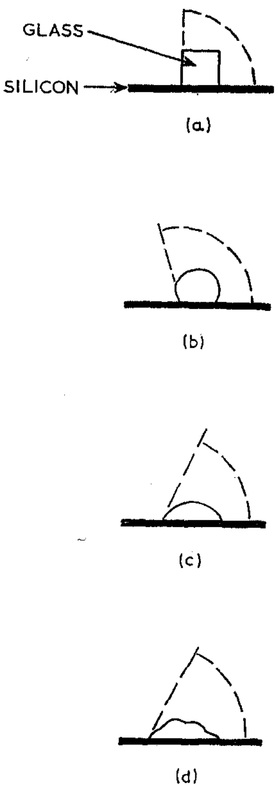

Figure 4 Sequence of variation of contact angle of glass on silicon. (a) Initial stage, contact angle 90°. (b) First deformation, contact angle > 90°. (c) Wetting, contact angle < 90°. (d) Bubbling, contact angle still < 90°.

fusion temperatures as starting points for firing trials on preoxidised silicon. Preliminary trials showed that the compact fusion temperature and the fusion temperature for a particular glass-ceramic on silicon were generally similar, as given in table I. This test was accordingly used to obtain an initial idea of the fusion temperatures for the majority of the materials thought to be suitable for application to preoxidised silicon.

N-type silicon slices approximately 2.5 cm diameter × 0.025 cm thick were degreased and then preoxidised by heating at a temperature of 1100° C for 3 h in an atmosphere of wet argon using the method described by Ainger [3]. Glass powder was prepared as described above and made up into suspensions generally using methylated spirit as the carrying medium. The suspensions were applied to the preoxidised silicon using a flow coating technique. The powder coating on the silicon was allowed to dry and the powder-coated silicon slices were placed in a tube furnace through which was passed an atmosphere of dried, high purity argon. The furnace temperature was raised at a rate of 5° C/min to the appropriate fusion temperature for each material (see table I) and this temperature was maintained for 5 min to fuse the coatings. The coating was also devitrified in this process. The temperature was then allowed to fall at the natural cooling rate of the furnace, the samples being maintained in the protective atmosphere throughout the firing. Initially, firings were carried out at the compact fusion temperatures but improved coatings usually resulted when the firing temperature was a little lower than this. Too high a firing temperature resulted in blistering of the coatings and this was believed to result from the glass-ceramic penetrating the silicon dioxide interlayer and reacting with the underlying silicon. The glass-ceramic coatings on the preoxidised silicon were white, smooth, free from cracks and were adherent to the silicon when fired at the temperature given in table I for a period of 5 min. Further coating trials with the various glass-ceramics showed that the firing temperatures could be reduced significantly (by up to 50° C) although it was necessary to increase the time held at this lower temperature to $\frac{1}{2}$ h in order to obtain satisfactory coatings on the preoxidised silicon.

The coating thicknesses were generally 50 to 75 μm. It was found to be possible to reduce this to 25 μm or less by reducing the particle size of the powder by further milling to substantially less than 10 μm.

Concurrently with the coating work described above, bonding trials have been carried out. The procedure was to stack powder-coated slices of silicon in a suitable jig and fire under a suitable load (provided by a molybdenum cylinder) to the conditions determined in the coating trials, i.e. to the temperature generally as given in table I. The silicon slices were found to be firmly bonded together and the bonding material was almost completely free of bubbles. Examples of silicon slices bonded with glass-ceramic are shown in fig. 5.

4. Examination of the Coated and Bonded Silicon [4]

N-type silicon slices, coated as described above, were examined to ascertain the extent of damage to the silicon by the glass-ceramics and to determine whether any of the glass-ceramic constituents had diffused into the silicon to a sufficient extent to convert the silicon to *p*-type. The glass-ceramic coatings and intermediate

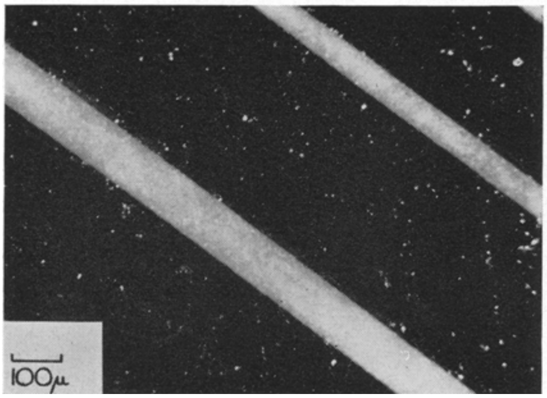

Figure 5 Silicon slices bonded together with glass-ceramic No. 18 (× 61).

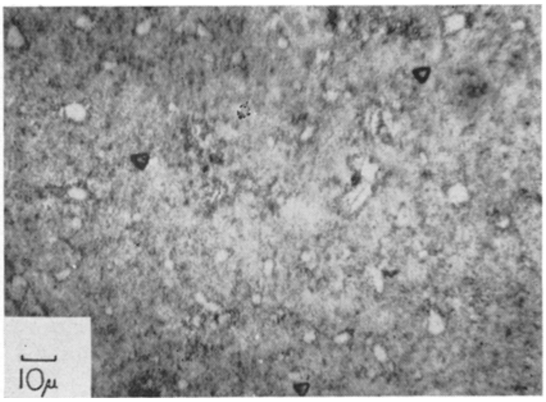

Figure 6 Glass-ceramic No. 13 on silicon (coated at 1230° C/5 min). Photomicrograph of the underlying silicon surface shows the presence of triangular dislocation etch pits revealed by acid etching. Silicon not coated with glass-ceramic has very few dislocation etch pits.

oxide layers were removed from the silicon by etching in 40% hydrofluoric acid. The silicon slices were then examined using standard grooving, etching and staining techniques.

Grooves were cut in the surface of the slices, and the grooves and surrounding areas stained with a copper sulphate/hydrofluoric acid stain. This stain is preferential and affects only *n*-type silicon, so any *p*-type silicon is unstained and easily visible under a microscope. The depth of any *p*-type layer was determined by microscopical examination.

Slices were also etched in a solution comprising one part 48% hydrofluoric acid, three parts concentrated nitric acid and six parts glacial acetic acid, and then examined microscopically for dislocations and the presence of slip damage. Typical examples of triangular dislocation etch pits are shown in fig. 6.

The results of the examinations showed that with all the glass-ceramics it was necessary to use an intermediate oxide layer in order to prevent diffusion of the glass-ceramic constituents into the silicon. Damage to the silicon was heavy where this interlayer was omitted. The various glass-ceramics attacked the silicon underlying the oxide layer to different extents, depending on composition of the glass-ceramic, fusion temperature of the glass-ceramic onto the preoxidised silicon and the thickness of the intermediate oxide layer. It was shown that reduction in the fusion temperature of a glass-ceramic on preoxidised silicon by about 50° C, decreased the extent of the attack by the coating on the underlying silicon, even though the fusion time had to be increased at the lower temperatures. Thinner oxide layers were also more effective as barriers at the lower fusion temperatures than at the higher fusion temperatures. For example, at the temperatures where fusion was satisfactorily completed in 5 min (given in table I) an oxide thickness of 1 μm was necessary, and in many cases an oxide thickness of 1.3 μm was required, but with the lower firing temperatures for which a 30 min fusion period was necessary an oxide thickness of 0.5 μm was adequate for some glass-ceramics. This was the case for glass-ceramics Nos. 13 and 18, which were fired onto preoxidised silicon at a temperature of 1180° C and maintained for 30 min, using an intermediate oxide layer 0.5 μm thick, when the extent of damage of the underlying silicon was very light.

5. Conclusions

The work described in the present paper has shown that it is possible to prepare glass-ceramics, basically of the zinc alumino-silicate type with additions of calcium oxide, barium oxide or boric oxide, which are matched in linear thermal expansion characteristics to silicon and which can be applied satisfactorily to preoxidised silicon at temperatures in the region of 1200° C to give smooth adherent coatings, these being refractory to temperatures of at least 1100° C.

Such glass-ceramics can also be used to bond together silicon pieces using similar firing schedules to those used to provide the coatings on the silicon.

It has also been shown that by suitable choice of the firing conditions and the thickness of the silicon dioxide interlayer, the attack by the glass-ceramic on the underlying silicon can be reduced to a negligible extent.

The glass-ceramics have high volume resistivities (greater than 10^8 ohm cm at 500° C) and can resist the environmental conditions likely to be encountered in diffusion processes.

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