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The Formation and Devitrification of Oxides on Silicon

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The thermal oxidation of silicon in various gaseous atmospheres has been studied and the growth rate data and activation energies determined. The oxide layers contained defects, the density of which increased with increasing temperature and time; microcracks were also observed. The devitrification of these oxides was studied at 1300° C and above in argon-oxygen atmospheres; water vapour was found effectively to catalyse the process. Sections of the devitrified oxide were prepared and examined with an electron microscope and electron diffraction patterns recorded. The latter exhibit a probable cubic structure, cell size 8.16 Å, which does not correspond to any published structure of crystalline silica. The formation of a "rosette" structure was also observed and was probably a stress-relief phenomenon. The origin of the rosette structure was traced to the Si-SiO_2 interface and revealed by controlled removal of the oxide layer.

1. Introduction

The surface of silicon may be oxidised to give thin dense films of silicon dioxide. This oxide film has been extensively used in silicon planar technology as a mask against certain impurities, e.g. boron and phosphorus, as a junction passivator and as a dielectric. In certain silicon solid circuits, a deep boron diffusion is used for isolation, and this necessitates an oxide layer between 1 and 2 microns thick for masking the rest of the device area against diffusion of boron. In order to achieve this isolation diffusion, the oxide film has to survive thermal cycling up to 1200 to 1300° C for long periods of time.

The oxidation of silicon is usually carried out in an atmosphere of either steam, wet oxygen or argon, or dry oxygen in the temperature range 900 to 1200° C. Sometimes a combination of atmospheres is used by alternating from one to another during growth.

The above oxidation systems were studied and the relevant rate data determined. The conditions necessary for the growth of an oxide which neither devitrifies nor contains other crystal defects after further high temperature processing were investigated.

2. Growth and Properties of Oxides on Silicon

2.1. Experimental

2.1.1. Apparatus

The oxidation system, diagrammatically shown in fig. 1, consisted of a high temperature diffusion type furnace fitted with a fused quartz reaction tube and feed lines. The steam generator and gas saturator were also constructed in fused quartz and linked to the fused quartz feed lines and taps with PTFE (Beckman) couplings; the feed lines and taps were heated with tape and maintained at 140 to 150° C. All rotameters were calibrated and gas pressure corrections made for flow rate. The incoming gases were dried with molecular sieves contained in stainless steel tubes.

The hot zone of the furnace was profiled under flow conditions and found to be flat to 5° C over a length of 4 in. The reaction tube was made so that the steam or wet gas was carried through the furnace hot zone before issuing into it, to avoid condensation and spitting.

The steam generator was designed with two heater windings (see fig. 2), one outer one,

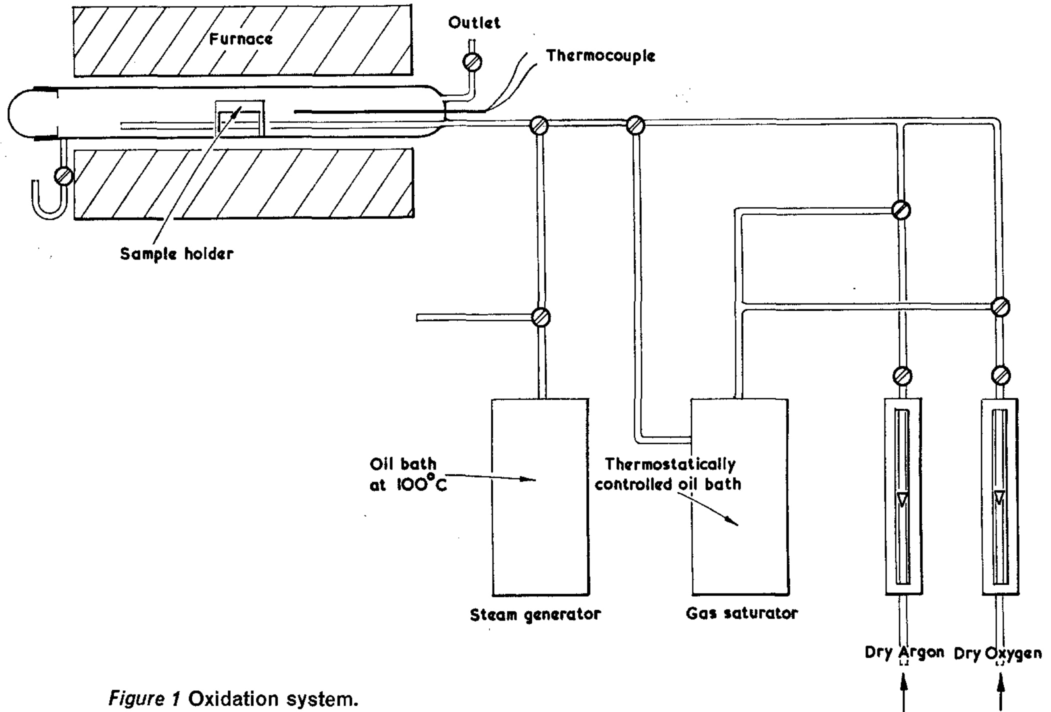

Figure 1 Oxidation system.

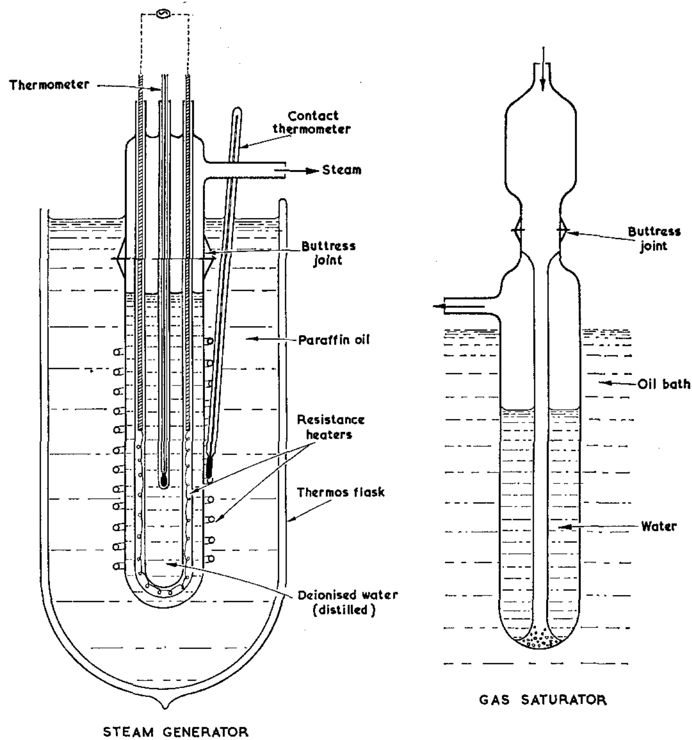

Figure 2

which was regulated to maintain about 99 to 100° C in the evaporator without boiling, and an inner one, the power to which controlled the flow rate of steam.

2.1.2. Method

The silicon substrates were n-type, Czochralski-pulled (resistivities 0.1 to 10 ohm cm), cut on the (111) plane and finally polished on diamond (0.25 to 1 μm paste) to give a mirror finish. Chemically polished slices were also prepared and simultaneously used in oxidation runs. P-type substrates were also used later for comparative tests of the dielectric strengths of oxides grown onto p- and n-type silicon. It is reported by various authors [1, 2] that there is no difference statistically for the growth rates obtained for n- and p-type materials. The polished slices were cut into smaller pieces (10 × 5 and 20 × 5 mm), carefully cleaned, dried and loaded into a covered fused quartz jig plate. The jig was slid into the furnace at temperature in a purge of argon. The furnace end was closed and the jig was allowed to come to equilibrium with the furnace temperature (usually 10 min) as indicated by the reading of the thermocouple adjacent to it.

Steam was generated at the rate 500, 1000 or 2000 ml/min and allowed to run to waste. When the jig had reached the furnace temperature, the argon flow was switched off and steam was passed through for the appropriate times. At the end of each run the steam was switched to waste and the system flushed with argon. The jig was withdrawn to the cooler end of tube and unloaded.

In the case of dry oxygen oxidation the purging gas, argon, was replaced by oxygen at flow rates 500 to 1000 ml/min; after each run the system was again purged by argon.

For oxidation with wet argon, the gas was switched from the purging condition to one of oxide growth, by passing it through the saturator controlled at some predetermined temperature. Similarly oxygen was passed through the saturator for growth of oxides in wet oxygen.

2.2. Results

Four specimens were used each run, for evaluation of the properties, reproducibility and uniformity of the oxide films. Two films (mechanically polished) were used for thickness measurements and dielectric strengths, one for weight measurements, and the last (usually chemically polished) for microscopic examination and any further experiments. The slices used for thickness measurements were masked and part of the oxide layer removed by an HF etch. The thickness measurements were made with a Taylor-Hobson "Talysurf"; the readings were accurate to 50 Å. Immediately before oxidation the specimens used for weight determinations were weighed on a Cahn micro-balance with an ultimate sensitivity of 0.1 μg. The specimens were weighed after oxidation and again after the oxide had been removed by an HF etch and the oxide density and the oxidation efficiency were calculated.

The dielectric strengths of the oxide films were determined using the Rohco "Anodicator". A small ball probe is positioned on the oxide surface and contact made to the silicon substrate. A 50 c/sec field is applied starting at zero volts and increases at a uniform rate until breakdown occurs; the voltage at which it occurs is automatically recorded.

The oxide films formed upon chemically polished substrates were heated at 900° C for 2 to 5 min in a chlorine atmosphere diluted to 2 to 5% with pure argon. This is a sensitive method [3] for indication of the imperfections in the oxide layers.

2.2.1. Rate Data

After the completion of a number of runs at different temperatures and various times for a given set of conditions (e.g. 1000 ml/min of steam) the results were plotted and analysed. A comprehensive set of data curves were drawn and typical log-log plots of thickness versus time for dry oxygen and steam are shown in figs. 3 to 5. The results are the mean of the average measurements of two individual slices (i.e. several readings of the oxide step of each slice were made, the average taken and the mean of the averages of two slices calculated). It was found that the difference between the oxide thickness of similarly treated slices was never greater than ±4% but normally considerably less.

In the flow rate range of 500 to 2000 ml/min for steam no significant difference in growth rate at a given temperature was found. In subsequent experiments, the growth of oxides in steam was carried out at a flow rate of 1 l/min. The same flow rate 1 l/min was used (for practical convenience) for wet and dry gas systems and the rate data quoted are for this.

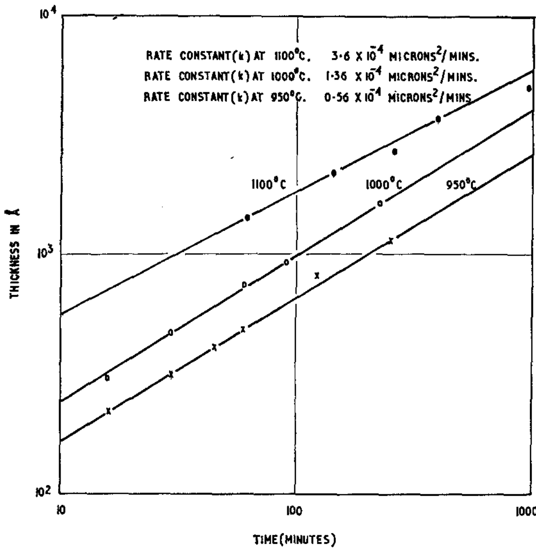

Figure 3 Oxidation with dry oxygen.

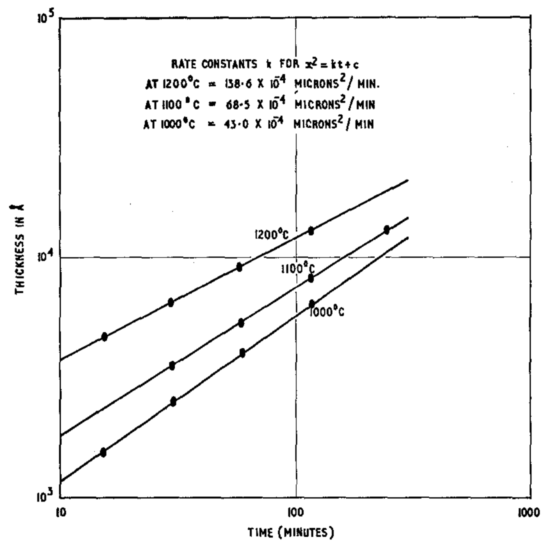

Figure 4 Oxidation of epitaxial silicon n/n$^+$ in steam.

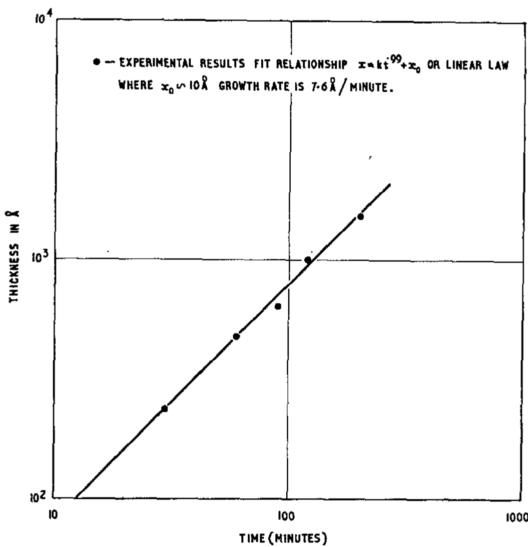

Figure 5 Oxidation with steam at 800° C.

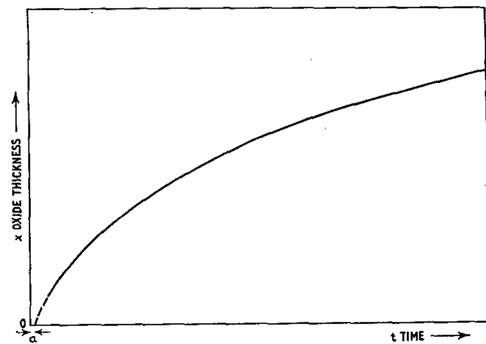

Figure 6 Parabolic growth rate.

It was found that the rate constants (see table I) for steam were the highest and those for dry oxygen the lowest for the same temperature in the range 1000 to 1200° C. Oxygen and argon saturated with water vapour at different temperatures gave rate constants less than those for steam but higher than those for dry oxygen. They were less than those quoted by other authors, suggesting the gas was not fully saturated with water vapour at the specified temperature. The growth data for 1000 to 1200° C were plotted, for convenience of reading off results, on a log-log scale (figs. 3 to 5) and give straight line relationships. The slopes of these lines approach 0.5, thus indicating that the growth obeys a parabolic law of the form

$$x^2 = kt + C$$

where x = oxide thickness
t = time
C = constant

If the results are now plotted as x^2 vs t, fairly good straight line relationships are obtained confirming the parabolic growth rate behaviour.

However the results indicate, by a deviation from the slope of 0.5, that they may not obey a purely parabolic law for *short* growth times. If the data are plotted as x vs t we obtain curves such as fig. 6, for which the following type of

TABLE I Growth rate data for the oxidation of silicon

Oxidation system	Temperature (° C)	Rate constant
Dry oxygen	950	0.56×10^{-4} μm^2/min
Dry oxygen	1000	1.36×10^{-4} μm^2/min
Dry oxygen	1100	3.60×10^{-4} μm^2/min
Wet oxygen (H_2O, 90° C)	995	13.6×10^{-4} μm^2/min
Wet oxygen (H_2O, 90° C)	1095	26.8×10^{-4} μm^2/min
Wet oxygen (H_2O, 90° C)	1200	57×10^{-4} μm^2/min
Wet argon (H_2O, 90° C)	1200	57×10^{-4} μm^2/min
Wet argon (H_2O, 95° C)	1100	56.4×10^{-4} μm^2/min
Wet oxygen (H_2O, 95° C)	1100	57×10^{-4} μm^2/min
Steam (1 l/min)	800	7.6×10^{-4} μm/min
Steam (1 l/min)	1000	43×10^{-4} μm^2/min
Steam (1 l/min)	1065	70×10^{-4} μm^2/min
Steam (1 l/min)	1200	156×10^{-4} μm^2/min
Steam (1 l/min)	1000	43×10^{-4} μm^2/min
for n/n$^+$ epitaxial	1100	68.5×10^{-4} μm^2/min
wafers	1200	138.6×10^{-4} μm^2/min

analysis can be carried out.

The parabolic curve, i.e. the predominant curve, can be continued to intersect t when $x = 0$ at some value a. Now the parabolic curve can be defined as

$$x = K_p\,(t^{\frac{1}{2}} - a^{\frac{1}{2}})$$

and the initial linear part as

$$x = K_l t$$

where K_p = parabolic rate constant
K_l = linear rate constant
x = oxide thickness
t = time

The value a can be more conveniently obtained by plotting the data as x vs $t^{\frac{1}{2}}$ and finding the intercept at x on the $t^{\frac{1}{2}}$ ordinate. The changeover from a linear to parabolic law will occur when the slopes are equal, i.e.

$$\frac{dx}{dt} = K_1 = \frac{K_p}{2t^{\frac{1}{2}}}$$

When this occurs, x (oxide thickness) can be expressed by

$$x = K_l t = K_p\,(t^{\frac{1}{2}} - a^{\frac{1}{2}})$$

or substituting the value of K_1 from above

$$\frac{Kp}{2t^{\frac{1}{2}}}\,t = K_p\,(t^{\frac{1}{2}} - a^{\frac{1}{2}})$$

from which

$$t^{\frac{1}{2}} = 2a^{\frac{1}{2}} \text{ or } t = 4a$$

Using this relationship the results in table II were obtained.

The results indicate that at the lower temperatures of oxide growth, for both wet and dry oxygen, the inital growth could be linear with time but rapidly becomes parabolic, i.e. diffusion-controlled. They also show that the thicknesses of oxide produced in the stated systems at the turnover point, i.e. $t = 4a$ are of the same order of magnitude but not the same value. One might anticipate the same thickness of oxide for the turnover point for different temperatures. In order to obtain a value of K_l, the initial rate constant, two methods are available. The first comes from that already described

i.e. when $$\frac{dx}{dt} = K_1 = \frac{K_p}{2t^{\frac{1}{2}}}$$

when $$t = 4a$$ $$t^{\frac{1}{2}} = 2a^{\frac{1}{2}}$$

from which $$K_1 = \frac{K_p}{4a^{\frac{1}{2}}}$$

and substituting values obtained for wet oxygen (90° C, H_2O) of

$$K_p = 370 \text{ Å/min}^{\frac{1}{2}} \text{ and } a^{\frac{1}{2}} = 1.56$$
$$K_1 = 60 \text{ Å/min}$$

Another method for analysing the data to determine K_1 is due to Jost [4]. He suggests, for simplicity, that reactions of the type, which initially have a linear time dependence and then

TABLE II

Type of oxidation	Temperature (° C)	$t = 4a$	Thickness of oxide when growth becomes parabolic
Dry oxygen	950	9 min	100 Å
Dry oxygen	1000	9 min	175 Å
Dry oxygen	1100	0.01 min	25 Å
Wet oxygen (H_2O, 90° C)	995	9.7 min	590 Å
Wet oxygen (H_2O, 90° C)	1200	1 min	450 Å
Steam	1000 to 1200	0	—

become parabolic, can be considered as two reactions in series and written as such.

The initial linear law is

$$x = K_1 t$$

and the parabolic law is

$$x = K_p t^{\frac{1}{2}}$$

The reaction resistivities x/K_1 and $x^2/K_p{}^2$ are additive, giving

$$\frac{t}{x} = \frac{1}{K_1} + \frac{x}{(K_p)^2}$$

Again using the results from wet oxygen (90° C, H_2O) at 995° C and plotting t/x vs x the intercept on the t/x axis was determined to give $1/K_1$ at $x = O$ whilst the slope gave $1/K_p{}^2$. The results were as follows:—

$$\frac{1}{K_1} = 0.0098 \therefore K_1 = 100 \text{ Å/min}$$

$$\frac{1}{(K_p)^2} = \frac{0.00336}{500} \text{ or } (K_p)^2 = 14.9 \times 10^4 \text{ Å}^2\text{/min}$$

$(K_p)^2$ from plot of x vs $t^{\frac{1}{2}}$ gave 13.6×10^4 Å^2/min

Although the absolute values of each analysis differ they can be considered to give the order of the rate constant for the inital linear growth rate.

One significant result obtained was for steam oxidation at 800° C. The data for these conditions obey a linear law since the slope of the line on the log-log plot was 0.99. Recently Flaschen *et al* [2] found a slope 0.8 but this was determined by only two data points. One might speculate that with more data he too would have found a slope approaching unity.

J. Sladkova [5] also in a recent paper on oxidation of silicon with dry oxygen showed that a linear law was obeyed from 600 to 950° C and a parabolic one above 950° C.

The rate constants indicated in table I were plotted against the reciprocal of absolute temperature and an overall activation energy determined for each of the various systems examined over the temperature range 1000 to 1200° C. The activation energies shown in table III agree fairly well with those of Deal [1] and Flaschen [2].

Our results suggest that in the higher temperature range 1000 to 1200° C that the oxide formation is diffusion controlled whereas at 800° C in steam it may be surface or interfacial reaction controlled since it behaves as a linear law. No attempt has been made to determine the nature of the diffusing species but recent work by Jorgensen [6] and Ligenza [7] suggest that it is a charged species.

2.2.2. Oxidation Efficiency and Density

The oxidation efficiences were calculated for oxides grown in steam and dry oxygen as outlined above. It was found that it was unity in the case of dry oxygen and between 0.95 and 0.98 for steam.

The oxide densities were calculated from weight measurements and thickness data and found to range from 2.20 to 2.25 for dry oxygen and 2.05 to 2.17 for steam oxidation although the majority of the latter were in the 2.10 to 2.15 range.

2.2.3. Dielectric Strengths

The dielectric breakdown fields were calculated for a number of oxides grown under different conditions. It was found that most oxides of thickness greater than 2000 Å had breakdown strengths between 4 and 6 MV/cm. Table IV indicates a range for differently prepared oxides on n- and p-type substrates. Although there are certain anomalies the most dense oxides (grown

TABLE III Activation energies for different types of silicon oxidation in temperature range 1000 to 1200° C

Type of oxidation	Activation energy in Kcal/mole		
	This report	Deal [1]	Flaschen [2]
Steam	24.3	20	18.4
Steam (epitaxial n/n^+)	21.7	—	—
Wet oxygen (H_2O, 95° C)	—	20.8	—
Wet oxygen (H_2O, 90° C)	20.4	—	—
Dry oxygen	29.8	30	30.6

in dry oxygen) exhibited the highest dielectric strengths.

The method is being modified so that a needle probe can be used, since it is desirable to reduce the area of contact and therefore the probability that a defect in the oxide is in the region of examination.

2.2.4. Appearance of Oxides

The oxides grown on silicon under the conditions mentioned appear to be very uniform from the interference colours they exhibited. (It has been found that when accurate rate data are not required, then the interference colours give a good estimate, accurate to about 100 Å, of film thickness in the range 500 to 10000 Å, with the help of the colour chart of Pliskin and Conrad [8]). The oxides are characterised by small inclusions and defects, the density of which increase with increasing temperature and time (figs. 7 and 8). The nature of these is not fully understood. It was observed that when thin oxides, 500 to 1500 Å in thickness were grown onto badly scratched substrates, the oxide effectively decorated the surface markings. It has recently been demonstrated that oxides grown on epitaxial layers contained fewer defects and inclusions than any Czochralski pulled silicon substrates. It appears possible that the surface defects on the substrate giving rise to these inclusions and defects are considerably reduced during the cleaning in hydrogen at 1250° C prior to epitaxial growth and in consequence the number replicated on the surface of the epitaxial layer is small.

In order to differentiate between pinholes or gross defects and the defects or inclusions referred to in the last paragraph (figs. 7 and 8) the oxidised slice was heated at 900° C in a diluted atmosphere for 2 to 5 min. If pinholes or gross defects are present then the chlorine penetrates the oxide film and removes the silicon underneath (chlorine rapidly attacks and removes silicon as halide at 900° C). It was found that a large majority of oxides grown were impervious to chlorine etching.

TABLE IV Dielectric strengths of thermal silicon oxides

Method of preparation	Thickness of oxide	Breakdown field MV/cm for following substrate		
		2 Ωcm n	1 Ωcm p	> 100 Ωcm p
Dry oxygen	1500 Å	11.3	4.52	12.8
Dry oxygen	2750	5.8	4.2	8.7
Dry oxygen	5200	5.7	4.84	5.55
Steam	400	16 to 24	14 to 23	14 to 40
Steam	1500	6.14	4.6	6.9 to 13.6
Steam	3800	5.15	4.49	4.4
Steam followed	5400	4.55	5.03	5.48
by dry oxygen	6200	4.58	4.72	6.45

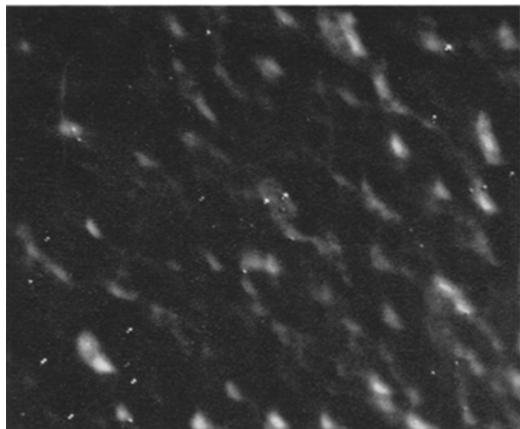

Figure 7 Silicon oxidised in steam at 1200° C/3.67 h (X137).

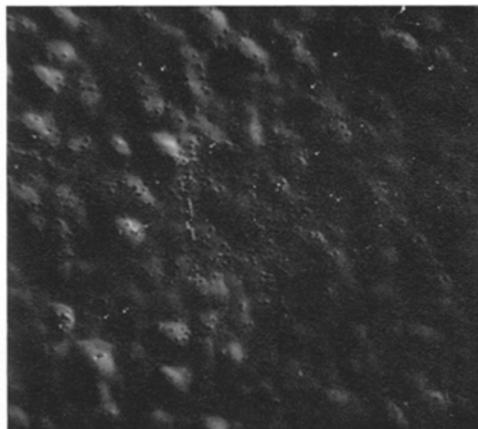

Figure 8 Above specimen after 1300° C/72 h in dry $Ar:O_2$ (X137).

Oxide windows were prepared by etching a small hole 2.5 to 4 mm in diameter in the back of the substrate with an HF etch and heating the slice at 900° C for 5 to 10 min in a dilute chlorine atmosphere. A typical result is shown in fig. 9. It can be seen that the oxide is buckled and indicates that it is in a state of compression as might be expected from the difference in the thermal expansions of silicon and vitreous silicon dioxide. The oxide windows were examined for presence of devitrified material or crystallinity, by X-ray and electron diffraction methods. No crystallinity was detected and only amorphous patterns of silica recorded.

2.3. Conclusions

It was confirmed that oxides grown in different atmospheres (steam, dry oxygen and wet oxygen) obey a parabolic growth law indicating a diffusion controlled reaction. The growth of oxide in steam at 800° C obeys a linear law but the reaction controlling mechanism is not known.

Good quality oxide films free from pinholes and crystalline defects were obtained from all systems, but where high growth rates are necessitated then the steam method is recommended. In order to minimise defects or inclusions in the oxide film scrupulous attention to cleaning and handling of slices is required. The ultimate way of achieving this would be to include *in situ* cleaning prior to the oxidation process. The best quality films were obtained on chemically polished substrates and epitaxial silicon slices. The oxidation efficiency for steam suggests that little or no oxide or silicon is eroded away during growth and that satisfactory dense films resulted.

3. The Devitrification and Formation of Other Defects in Thermally Grown Silicon Oxides

3.1. Introduction

The formation of devitrified areas (confirmed by electron diffraction as crystalline material) in the oxide glass on solid circuit chips occurred at the deep diffusion (isolation) drive in stage (1300° C/64 h in 100:1 argon:oxygen mixture). Immediately it was thought that this might be explained by the presence of the boric oxide glass left after the deposition stage but subsequent experiments with chips from which this glass had been removed proved to be negative. It was decided to study the behaviour of simple oxidised silicon slices at 1300° C for various long periods of time and the conditions for which devitrification readily occurred.

A brief word on the process of devitrification is relevant at this stage. It has been demonstrated by other workers that high purity silica glasses of low water content exhibit enhanced crystallisation in atmospheres containing oxygen and water vapour. Cristobalite is the phase normally observed. When cooled below 250° C it rapidly transforms into the α-phase resulting in a finely fractured material.

High purity silica glasses are sensitive to impurity pick-up; in particular a diamond lap leads to a rapid initial growth of cristobalite. Pretreatment with water can give a surface condition which exhibits enhanced crystallisation. Chemical analyses of silica glasses have shown the areas of devitrified glass (cristobalite) have higher concentrations of impurities, e.g.

Ca, Mg. Wagstaff [9] found that silica glass treated with an HF etch prior to thermal treatment in atmospheres containing oxygen or water vapour had surfaces which were difficult to nucleate. He has also carried out a series of experiments on the devitrification of vitreous silica glasses (high purity) and showed the following variables to be of great importance:

(a) Impurity content
(b) Water vapour content of atmosphere and glass
(c) State of reduction of glass
(d) Surface nucleation of the cristobalite phase.

A glass in the reduced state transforms very slowly compared with a stoichiometric one. If oxygen is present in the atmosphere the recrystallisation rate is increased and becomes controlled by the concentration of oxygen at the crystal-glass interface. Water vapour too acts as a source of oxygen and can weaken the glass by forming hydroxyls.

Later in the course of our work, another defect (non-crystalline) was observed in the oxide on solid circuit chips and conditions were simulated in the laboratory under which this occurred.

3.2. Experimental

The apparatus described for the steam oxidation was duplicated for devitrification experiments. However it was found that excessive devitrification of the high purity fused quartz reaction tube occurred, and it was replaced by a high purity alumina one fitted with a gas tight end cap (steel fitting). High purity dry argon and oxygen were used and for experiments where water vapour was intentionally introduced, the oxygen was bubbled through a water vapour saturator of the type shown in fig. 2 and the amount of water in the resulting argon-oxygen atmosphere determined by the temperature of the saturator.

The slices having 1.0 and 1.8 μm of oxide and solid circuit chips were mounted in a silicon holder and enclosed in a quartz carriage later replaced by an alumina boat. It was slowly pushed into the hot zone of the furnace tube under a purge of argon and the tube end then closed.

A series of runs was carried out at 1300° C in a dry argon-oxygen gas mixture (ratio 100:1) for times of 24 to 72 h. A further series were carried out in which water vapour concentrations of 300 to 2500 ppm were introduced into the furnace atmosphere.

3.3. Results

After the completion of each experiment the specimens were examined microscopically for evidence of devitrification. When this had occurred the slices were prepared with oxide windows as described earlier (fig. 9) for electron microscope and diffraction and X-ray diffractometer examination. Controlled etching and removal of oxide was achieved with a 5:1 NH_4F – HF etch at the rate of 0.22 μm/min.

3.3.1. *Devitrification*

It was found that heating both oxidised slices

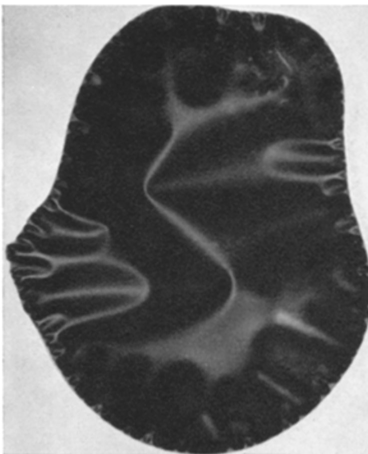

Figure 9 Oxide window (X54).

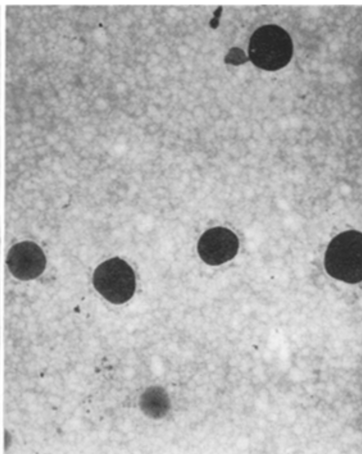

Figure 10 Devitrified areas 1300° C/2h in 2500 ppm water vapour (X4,500)

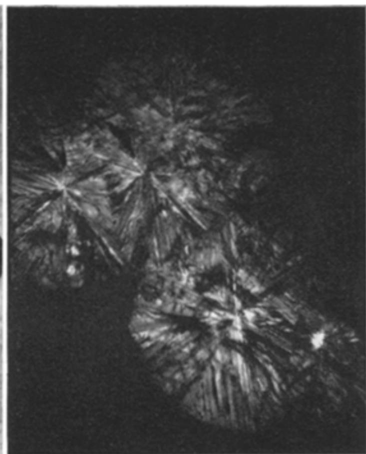

Figure 11 Devitrified areas 1300° C/64h in 2500 ppm water vapour (X1,800)

(1.0 and 1.8 μm of oxide) and solid circuit chips with and without the boric oxide glass in the dry argon oxygen atmosphere at 1300° C for periods of up to 72 h resulted only in an increase in the number of defects and/or inclusions referred to earlier (fig. 8). Evidence of devitrification as such was not observed microscopically and this was confirmed by electron microscope and diffraction examination of oxide windows suitably thinned for electron transmission. It was then decided to introduce water vapour into the argon-oxygen atmosphere to see if devitrification could be catalysed. In the first experiments 300 ppm of water vapour were introduced and specimens heated at 1300° C for 24 to 64 h. Excessive devitrification of the fused quartz ware resulted but little or none on the oxide of the silicon slices. However, when the water content was increased to 2500 ppm clearly defined devitrified areas were observed and their density (number/unit area) and size increased with time. Specimens containing these devitrified areas were prepared for electron microscope and diffraction studies. Some difficulty was encountered in preparing sections thin enough to give electron diffraction patterns. Two typical electron micrographs, shown in figs. 10 and 11, represent the result of heating for 2 and 64 h respectively, and diffraction patterns of these were also recorded. Better electron diffraction patterns were observed by devitrifying thin (0.1 to 0.3 μm) oxide layers and preparing these in window form for examination. The principal pattern observed was that of a probable simple cubic cell of lattice constant 8.16 Å. No evidence for cristobalite (the expected phase) was found in any of the specimens examined, i.e. oxidised silicon slices and solid circuit chips.

3.3.2. Other Defects

At some later stage in the work different defects were observed on certain solid circuit slices and appeared as crystalline "rosettes". Thin sections of these were prepared by chemical etching of the oxide with an $NH_4F - HF$ (5:1) etch and examination with electrons did not reveal any crystallinity in the film; highly defective regions were examined. A series of thermal cycling experiments in dry argon using oxidised silicon wafers gave the conditions under which the "rosette" defect type resulted, viz cycling to 1350° C for 6 to 8 h. Further examination of these defective wafers by electron diffraction methods gave no evidence of crystallinity. Typical areas on oxidised silicon slices are shown in figs. 12 and 13. A series of polaroid prints are shown in figs. 14 to 19 of a solid circuit chip exhibiting these oxide defects after

Figure 12 "Rosettes" initial condition (X375).

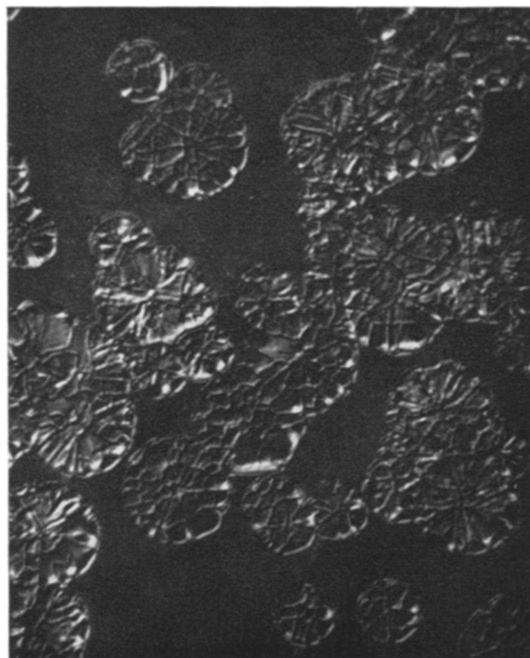

Figure 13 "Rosettes" after etching (X375).

various etch treatments:

Fig. 14 Initial surface of slice showing defective areas and isolation regions.

Fig. 15 After 0.1 μm of oxide had been removed.

Fig. 16 After all oxide had been etched away.

Fig. 17 After further etching with NH_4F:HF.

Fig. 18 After modified Dash etch for 40 secs.

Fig 19 After modified Dash etch for further 40 secs.

It is seen that the defective areas exist after oxide removal and this was confirmed also in the case of the oxidised slices. When silicon is removed from the chip, remnants of the defective regions are still clearly outlined in the silicon surface.

Talysurf prints of the surfaces after all the oxide had been removed by the NH_4F — HF etch indicated that the defects were standing up from the surface at a height approximately equal to original oxide thickness, i.e. 0.8 μm high in the case of the oxidised slices and 1.0 μm for the solid circuit chips. One might have anticipated that regions resistant to the etch were crystalline, having a much lower etch rate than the vitreous matrix. This however was not confirmed by electron diffraction patterns.

3.4. Discussion

Oxides thermally grown on to silicon contained defects which increased in density with increasing temperature and time. It had been established that when oxides on silicon are subjected to high temperatures in essentially argon atmospheres two deleterious effects are observed to take place.

The oxide devitrifies to give well defined crystalline areas when water vapour is introduced into the atmosphere of the furnace (maintained at 1300° C). The size of the crystallites increase with time, e.g. 20 and 30 μm diameter after 44 and 64 h respectively. The absence of cristobalite from X-ray and electron diffraction patterns is difficult to explain although it is suggested [10, 11], by other workers that mispacking of the SiO_4 tetrahedra can lead to large cell lattices.

The second defect, a rosette structure, although crystalline in appearance only appears when the oxidised specimens are heated at about 1350° C in a dry argon atmosphere. It was seen in fig. 9 that the oxide buckles and is in a state of compression. If we consider heating the oxidised slice 250° C above the temperature of oxide growth and for simplicity ignore the plasticity of the oxide and silicon then the differences in thermal expansion will give an oxide in tension and the cracking occurs as a stress relief phenomenon. It is under similar conditions that other thin films (evaporated) are reported to crack when a critical tensile stress is reached. This however may be an over simplification in the case of oxide on silicon although accounting for the experimental observations.

Since remnants of oxide still exist in the rosette areas after treatment with the modified Dash etch it appears probable that enhanced oxidation occurs in such regions. Impurities remaining in the silicon surface, e.g. lapping compounds could well catalyse oxidation by acting as oxide network modifiers resulting in higher diffusion rates of the oxidising species.

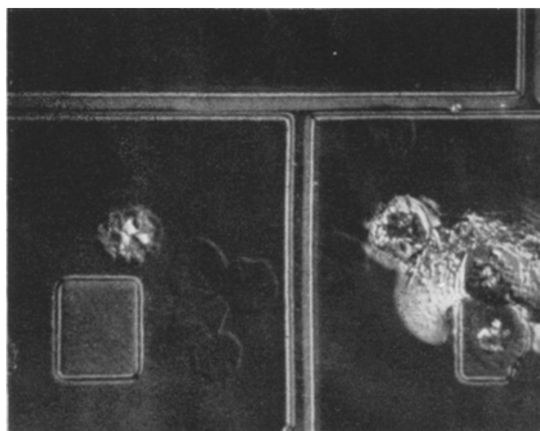

Figure 14 Initial surface of slice (X136).

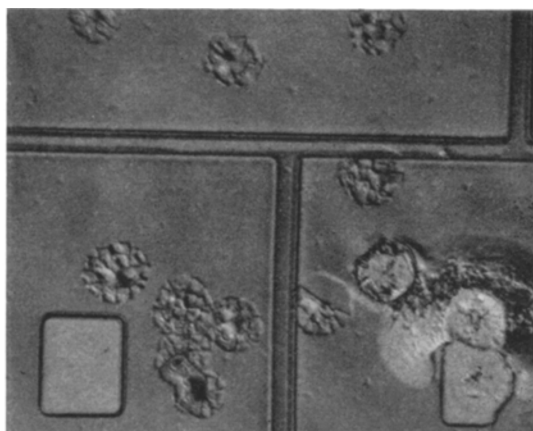

Figure 15 After 0.1 μm oxide removed (X136).

Figure 16 After all oxide removed (X136).

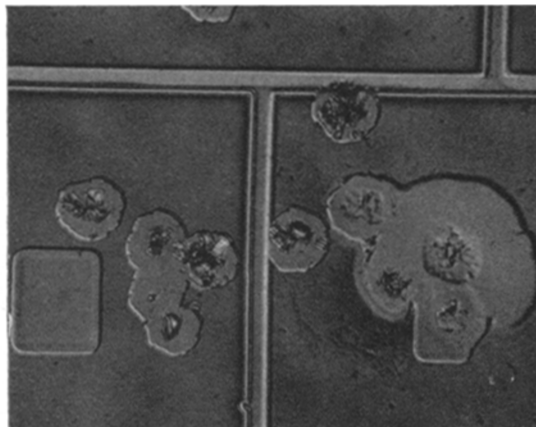

Figure 17 After further etching with NH_4F:HF (X136).

Figure 18 After modified Dash etch for 40 sec (X136).

Figure 19 After modified Dash etch for further 40 sec (X360).

3.5. Conclusions

It was found that two serious defects occur in the oxide film when it is subjected to high temperatures (1300 to 1350° C) and are harmful enough to prohibit device fabrication. The first defect is crystallisation of the oxide at nucleating centres, i.e. devitrification and is produced by the presence of water vapour in the furnace atmosphere. The second defect, the nature of which is not fully understood, is the "rosette" produced by heating at 1350° C in a dry atmosphere. Therefore it is essential that device engineers utilising oxides for deep diffusion processes at high temperatures should ensure that (a) the gases used are satisfactorily dried prior to entering the furnace tube and carried through impervious tubes (stainless steel) and (b) the furnace control is adequate, so that overshoots to 1350° C are eliminated.

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References

1. B. E. DEAL, *J. Electrochem. Soc.* **110(6)** (1963) 527.
2. H. C. EVITTS, H. W. COOPER, and S. S. FLASCHEN, *J. Electrochem. Soc.* **111(6)** (1964) 688.
3. M. M. ATALLA, "Properties of Elemental and Compound Semiconductors" Vol. 5, H. Gatos, Editor (Interscience Publishing Co, New York, 1960) p. 163.
4. W. JOST, "Diffusion in Solids, Liquids and Gases" (Academic Press, 1952) p. 353.
5. J. SLADKOVA, *Czech. J. Phys.* **B13** (1963) 452.

6. P. J. JORGENSEN, *J. Chem. Phys.* **37(4)** (August, 1962) 874.
7. J. R. LIGENZA, "Silicon oxidation in an oxygen plasma", Abstract No. 73, *Electrochem. Soc. Meeting* (Toronto; Spring, 1964).
8. W. A. PLISKIN, and E. E. CONRAD, *IBM, J. Res. and Dev.* **8** (1964) 43.
9. F. E. WAGSTAFF, "Kinetics of crystallisation of vitreous silica" (University of Utah, Ph.D., 1962).
10. V. G. HILL, and RUSTUM ROY, *J. Amer. Ceram. Soc.* **41(12)** (1958) 532.
11. W. EITEL, *Bull. Amer. Ceram. Soc.* **36(4)** (1957) 142.