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Surface treatments of silicon to enhance thermal nucleation

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We have investigated the physical characteristics and means of producing silicon surfaces treated to provide reliable nucleation sites for boiling in perfluorinated coolants. Three techniques may be used to provide these sites; removal of mechanical defects by liquid etchants; selective etching of one of the phases of a eutectic alloy; and deposition of an inert, porous material such as alumina. Consistent nucleation, required to assure proper heat transfer of silicon circuit chips, does not occur on polished silicon surfaces.

1. Introduction

In modern high-density semiconductor packaging technology, it is necessary to transfer heat from the surface of a heated semiconductor element to a heat sink at a rate high enough to keep the temperature within reasonable limits. One such technique for transferring heat is to immerse the semiconductor devices in a liquid, in this case a conventional perfluorocarbon. In operation, as the heat generated in the semiconductor device passes through the exposed surfaces, there is a rise in adjacent fluid temperature. This causes a local density change in the fluid and the generation of convection currents. The heat transfer process consists of conducting heat through the stagnant layer of fluid at the semiconductor surface, absorbing the heat in the fluid by virtue of its specific heat (for this fluid, 0.24), and removing the heat through the bulk motion of the fluid in convection. There is an approximately linear relationship between the heat flow and the silicon temperature in this regime. At a sufficient heat flow or with a properly prepared surface, boiling is nucleated at the surface, which leads to a departure from the linear relationship in the direction of reduced surface temperature. This occurs because of certain features of the boiling process. Initially, heat is absorbed directly at the surface of the silicon, by virtue of the latent heat of vaporization of the fluid, without having to pass through the stagnant fluid layer. Then, the departure of the bubble breaks up the stagnant layer, which permits fresh, cool fluid to come into direct contact with the silicon and, at the same time, encourages much more vigorous convection. Thus the characteristics of the surface, with respect to the initiation and support of the boiling process, are critical to the heat transfer process.

The topology of the surface required to nucleate boiling is complicated. A rough surface enhances nucleation; none of our clean, smoothly polished surfaces showed any tendency to nucleate. But both the degree and the character of the roughness of the surface necessary for nucleation still have to be determined.

To assure proper heat transfer at the interface, one must treat the exposed side of the device to provide reliable thermal nucleation sites. Since IBM mounts its chips with the circuit side facing the chip carrier, the exposed side is commonly referred to as the chip backside. This paper demonstrates the feasibility of three different techniques to provide these sites.

2. Experimental procedures

2.1. *Surface treatments*

The preliminary work was done on $2\frac{1}{4}$ in. Si wafers which were chemically polished on one side.

2.1.1. Mechanical treatment. A successful approach to mechanically roughen the surface was to sandblast it. This was done in a Vaporblaster*, using a standard multiperforated nozzle for 1–2 min, at a total pressure of 75 lb and with a

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* Product of Pressure Blast Mfg. Co.

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water slurry of 400 mesh alumina. The resulting surface had a uniform matte appearance. The sandblasted wafer was then thoroughly washed in distilled water and dried in a stream of dry nitrogen. The surface morphology is shown in Fig. 1.

2.1.2. Etchants. The effect of two preferential silicon etches was examined: the pyrocatechol-amine-water [1] and the potassium hydroxide etch [2]. The first etch was composed of 16 ml distilled water + 34 ml ethylenediamine + 6 g pyrocatechol. Etching was performed in a shallow beaker at 110° C for 2 min. After etching, the wafer was thoroughly washed in running water (~ 1–2 min). In the second etch, 5 N solutions were made in water and methyl alcohol, as well as in a 1:1 mixture of both. The effects of these solutions on silicon were evaluated at 50, 80 and 100° C; etch time was ~ 1–2 min in all experiments. In both etch systems, water acts as the acidic component towards silicon. Furthermore, both systems act similarly on smoothly polished silicon surfaces, forming four-sided pyramidal pits, which did not nucleate (Fig. 2). In a KOH etch, the presence of methyl alcohol or of propanol slows down the reaction rate. Hardly any etch pits were noted when there was a total absence of water. Fig. 3 shows the etch rates as a function of %KOH, aqueous KOH 5 N being about 23% [2].

Etching (with either etch) of a silicon surface into which defects were previously introduced – by sandblasting – produced the very complex surfaces of Figs. 4 and 5. As these photo-

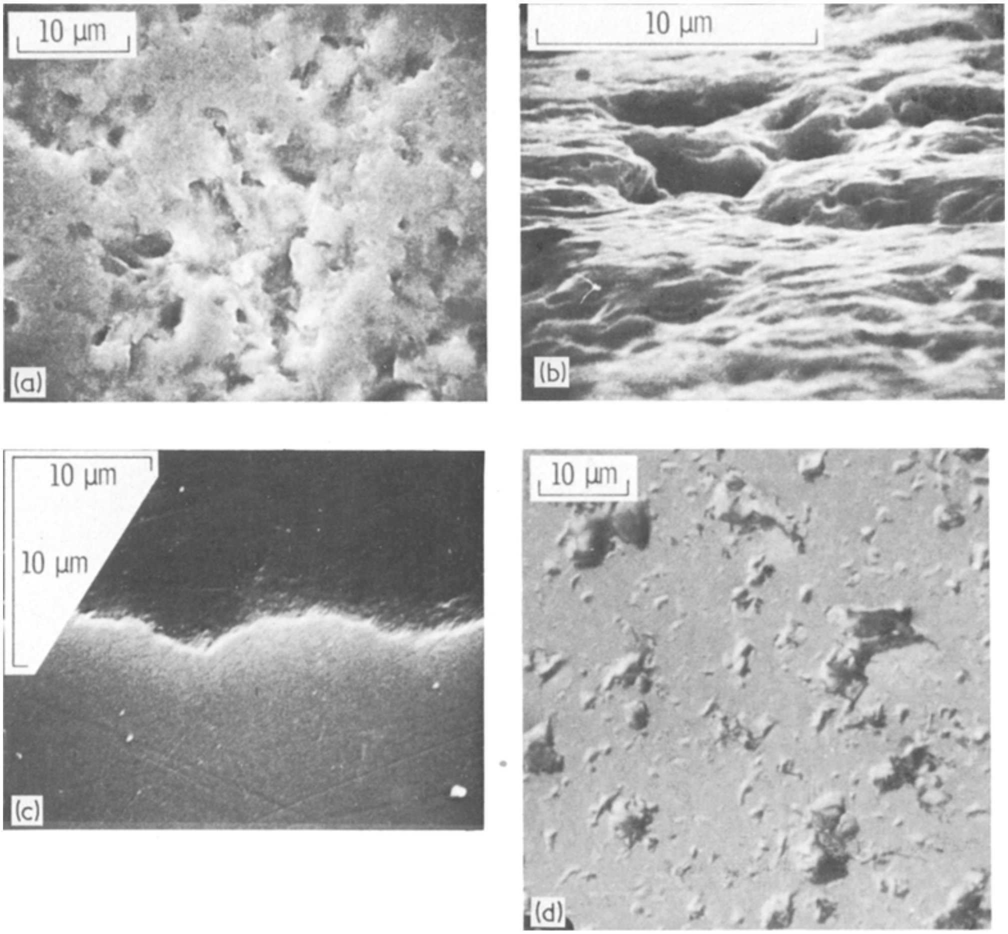

Fig. 1. Sandblasted silicon surface. (a) SEM, normal incidence. (b) SEM, oblique (80° from normal) incidence. (c) Polished × 1.5 angle section. (d) Interference contrast micrograph.

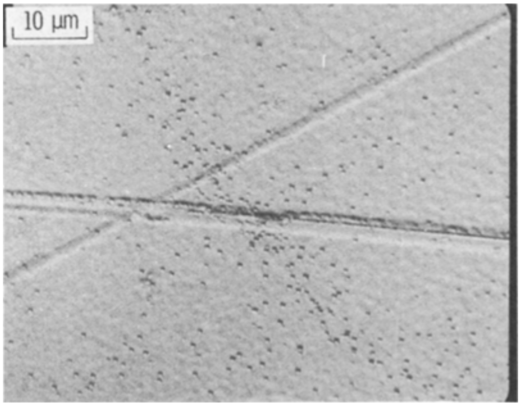

Fig. 2. Silicon surface etched with KOH/H_2O for 1 min. Interface contrast micrograph.

micrographs show, each etch on the same (1 1 0) orientation produced a different surface. Both surfaces nucleated.

This processing on silicon leads to questions about residual stresses in the wafer and contamination of the surface. X-ray topographs indicate that the sandblasting operation introduces a large amount of stress, as shown by the increased curvature of the wafer (Fig. 6b). After KOH etching (Fig. 6c), most of the stresses are relaxed, and the wafer appears the same as it did prior to treatment.

The other concern that sandblasting–KOH etching raises is the possibility of residue remaining on the intricate surface after the etch and water-rinsing step. No detectable potassium residue was noted by X-ray fluorescence analysis on KOH-etched Si wafers. Although this technique is only sensitive to 1 $\mu m\ cm^{-2}$, the measurement was not pursued any further at this time. KOH-etched Si wafers were leached in water at 55° C for 20 h. The pH of the water extract was ~ 5.5. Back titration of the etched wafers and standard gave equivalent values, indicating that there was no extractable alkali from the etched wafer.

Another technique [3] that was used to produce a complex surface was anodic etching without prior sandblasting. These surfaces, which nucleated well, have an intricate structure of narrow channels which run deep into the bulk of the wafer at 90° to the surface.

2.1.3. Eutectics. The feasibility of this technique was demonstrated by forming a silicon–gold eutectic [4]. When the gold domains are etched

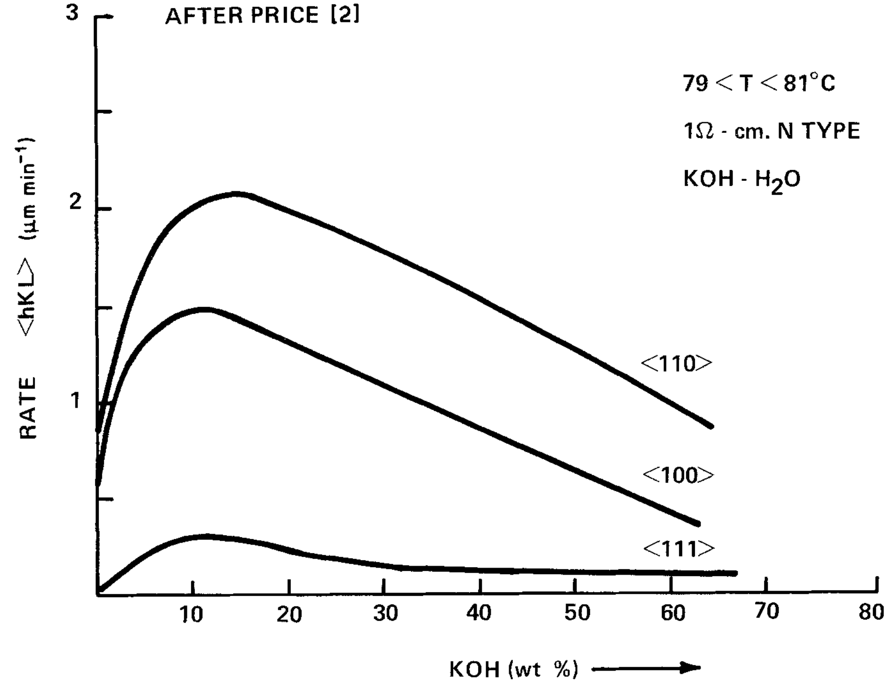

Fig. 3. Etching rate of KOH solution as a function of KOH concentration.

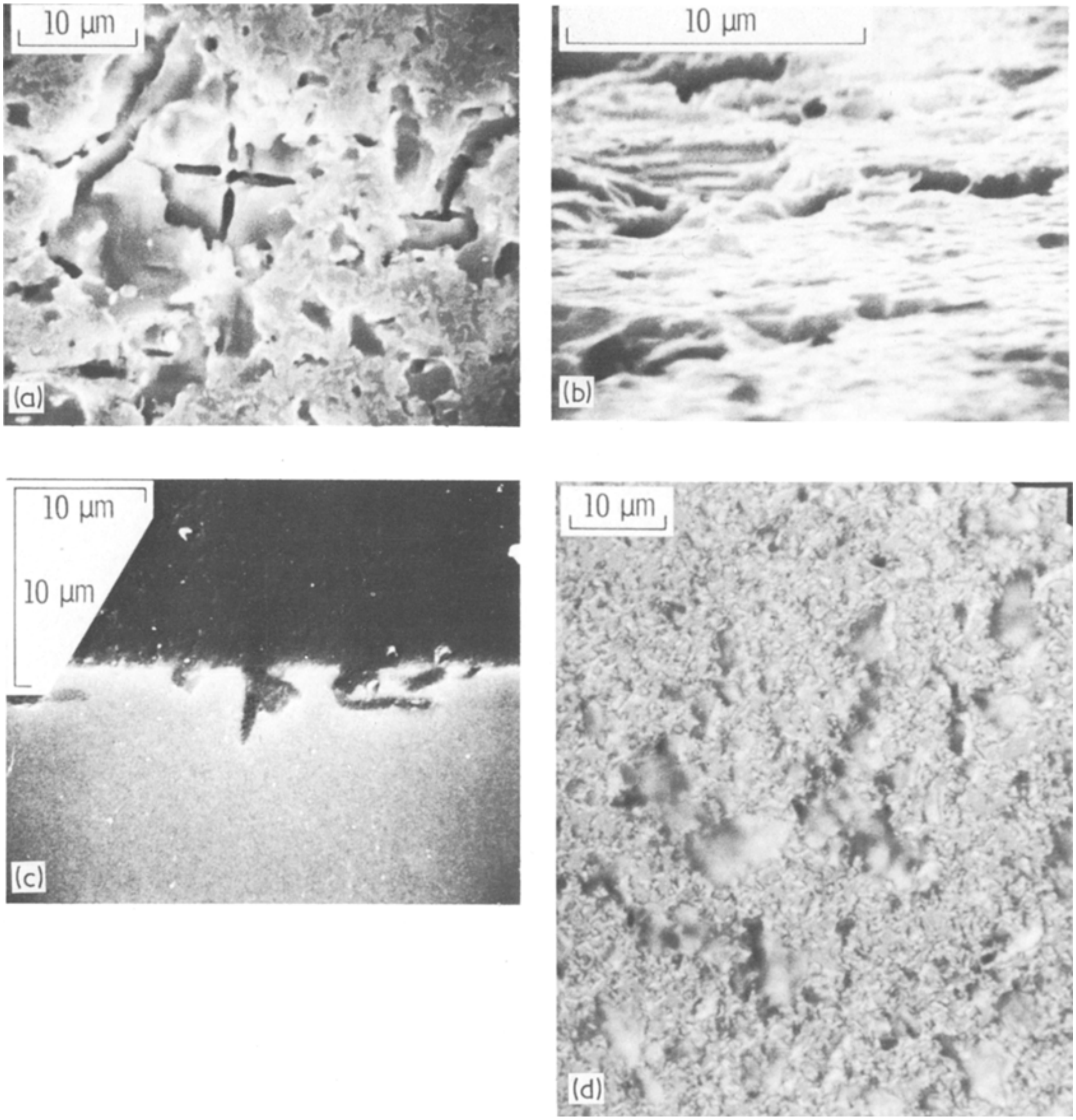

Fig. 4. Silicon surface sandblasted, followed by KOH/H_2O etch. (a) SEM, normal incidence. (b) SEM, oblique (80° from normal) incidence. (c) Polished × 1.5 angle section. (d) Interference contrast micrograph.

out, a uniformly pitted surface remains (Fig. 7). The gold domains run at an acute angle to the surface. An approximately 1 μm thick gold layer was deposited on the smooth side of the silicon wafers in a vacuum system. The substrate temperature during the deposition was ~ 200° C. The gold-coated wafers were placed in a muffle furnace in a nitrogen atmosphere at 400° C for 15 min and the furnace cooled to room temperature. The gold phase was completely removed by etching in KI/I_2 [5] for 40 min at room temperature. The resulting surface, while quite effective for nucleation, is fragile. Portions of the surface structure can be removed by gently rubbing with a cotton swab moistened with methanol. After this rubbing, the thermal performance of the surface deteriorates with the onset of boiling and requires a higher excess temperature than the 'unrubbed' surface.

2.1.4. Depositions. A high-lead, low-melting glass was pasted up with terpineol and applied to the silicon wafer. The terpineol was driven off on a

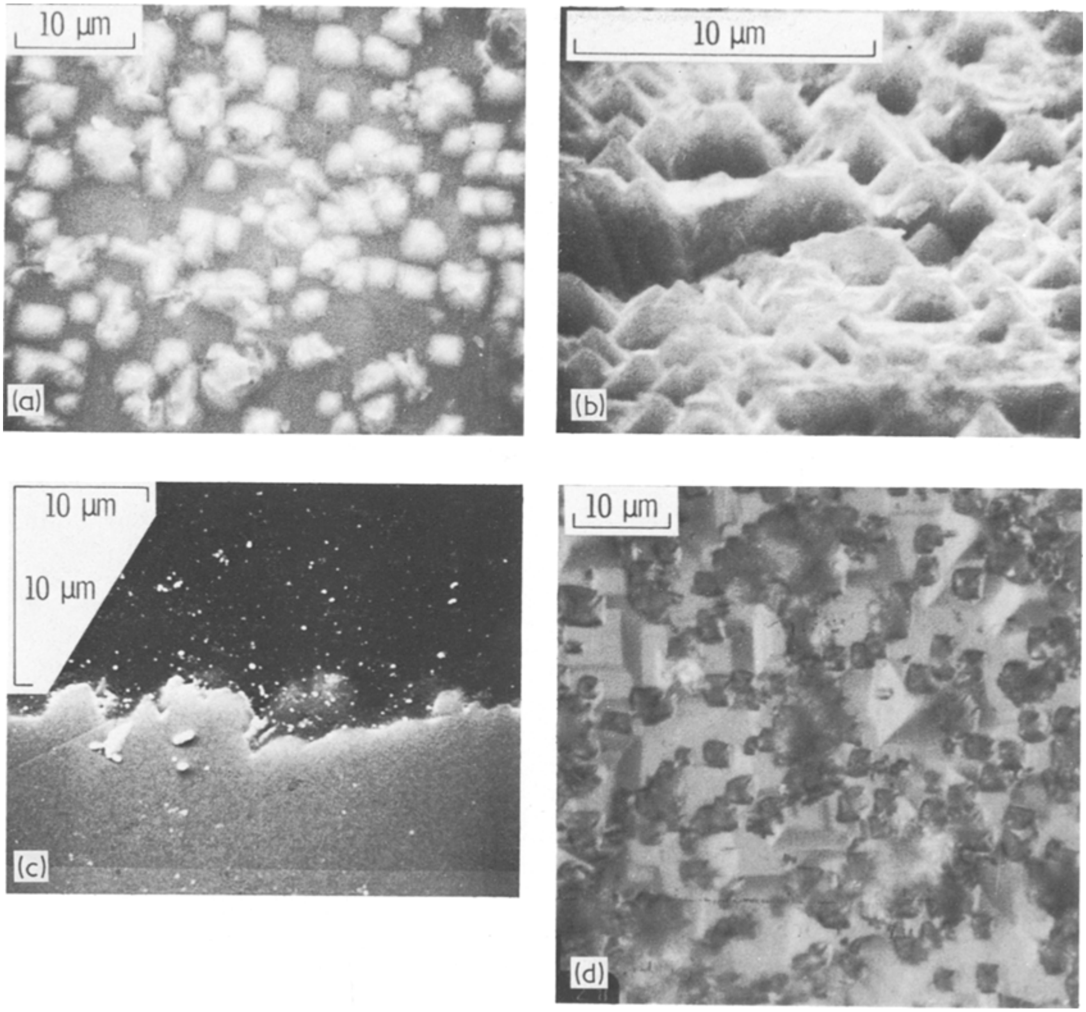

Fig. 5. Silicon surface sandblasted, followed by pyrocatechol etch. (a) SEM, normal incidence. (b) SEM, oblique (80° to normal) incidence. (c) Polished × 1.5 angle section. (d) Interference contrast micrograph.

hot plate at 150–200° C. The wafer with the dried slurry was placed in a muffle furnace in air and heated to 500° C for 3 h, then furnace-cooled.

The resulting surface was a highly porous sintered layer which did not spall off. Attempts with lower sintering glasses failed because their coefficient of linear expansion was too high, sufficient enough to crack the silicon wafer. The porous glass surface did nucleate extensively. Plasma spray techniques* were used to deposit porous coatings of alumina and tungsten carbide. These were effective nucleating surfaces if they were of sufficient thickness.

3. Results

The variously treated surfaces were examined in an apparatus which permitted us to observe the onset of nucleation. The degree of nucleation was estimated by counting the number of sites on the surface which formed bubbles in the liquid. Equally important was the ability of this apparatus to permit the measurement of heat transferred across that interface. The critical portion of the apparatus used for heat transfer measurements is shown in Fig. 8. The heat generated in source winding C is conducted across copper block A (25 mm diameter), through the wafer and into the surrounding fluid. Phenolic

* Plasma spray coating produced by General Plasma Associates, Bloomfield, Connecticut, USA.

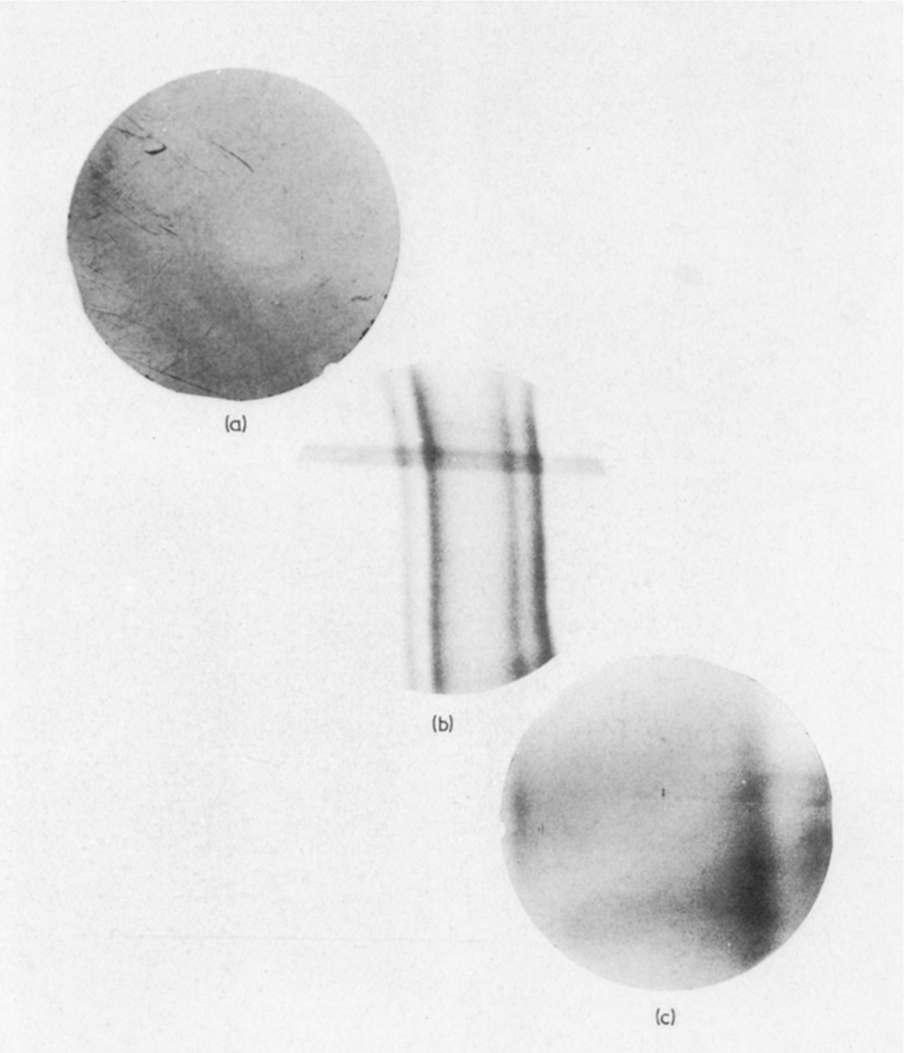

Fig. 6. X-ray topograph. (a) Silicon wafer. (b) Sandblasted silicon wafer. (c) Sandblasted and etched silicon wafer.

block D insulates the heater and controls the heat flow so that the bulk of it is through the wafer. Edge effects are eliminated by using a wafer that is substantially larger than the heat source. The exposed surface of the silicon wafer was viewed with a Zeiss Epi Techniscope, at magnifications up to × 40, to identify and count nucleation sites. The details of this apparatus, as well as the measurement techniques, are published separately [6].

Treated silicon surfaces can be organized into three groups representing three broad classes of thermal behaviour. The first group, including production-polished silicon surfaces, shows no tendency toward nucleate boiling within the power range available. The second group shows either limited nucleation capabilities or erratic behaviour. The third group of surfaces shows a high density of nucleation sites distributed uniformly over the surface.

3.1. *Group I – non-nucleating surfaces*

Within the power range available in this experiment, zero to approximately 2.4 W cm^{-2}, the conventional silicon surface used in chip tech-

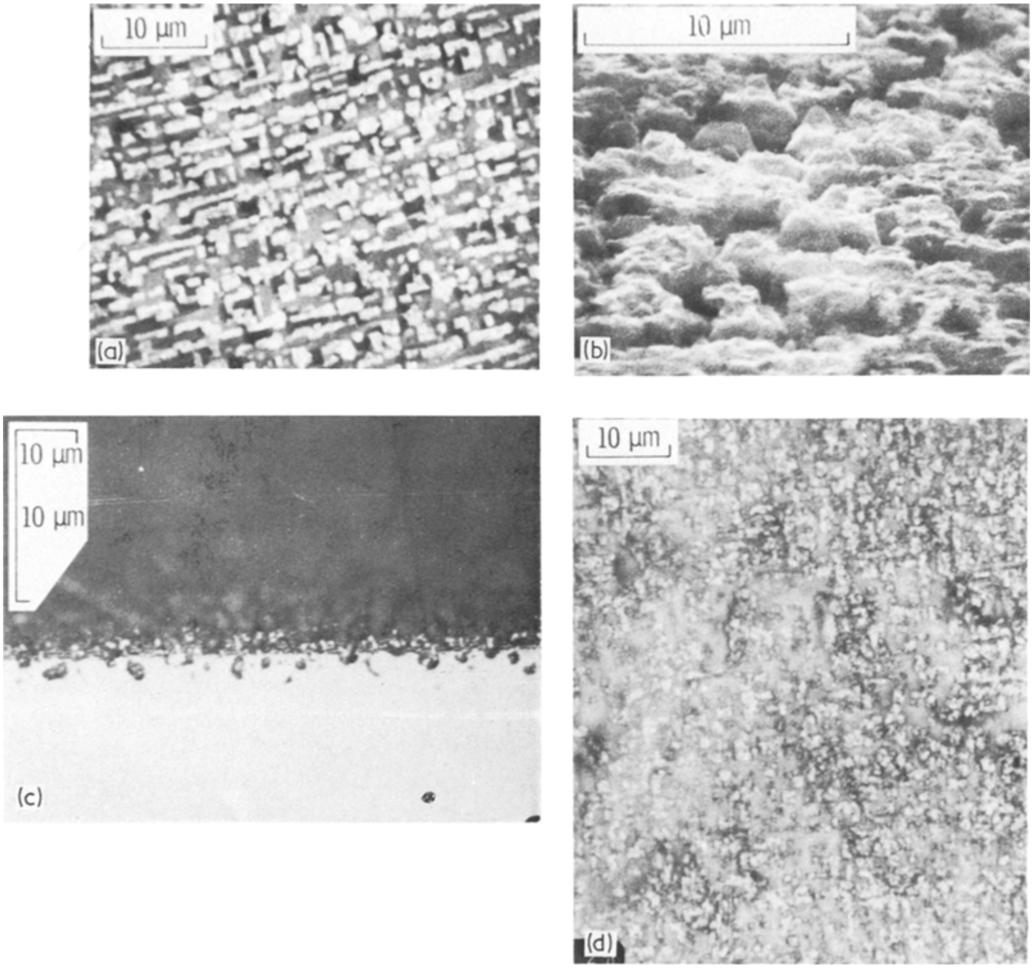

Fig. 7. Gold–silicon eutectic on silicon surface after etching with KI/I_2 to remove gold phase. (a) SEM, normal incidence. (b) SEM, oblique (80° to normal) incidence. (c) Polished × 3 angle section. (d) Interference contrast micrograph.

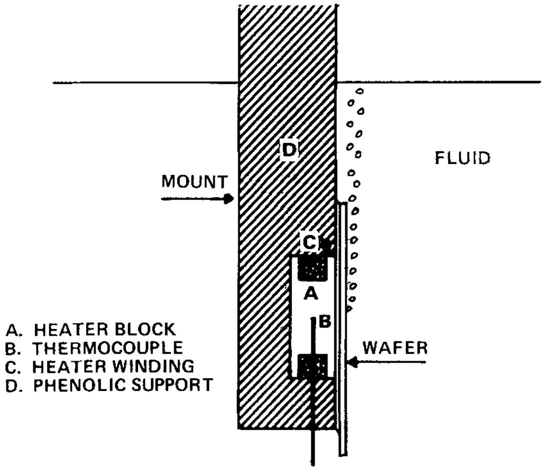

Fig. 8. Diagram of heat transfer apparatus.

nology would not nucleate when boiling in perfluorohexane (b.p. = 56° C). In one sample, the temperature rose to 102° C without boiling (hot enough to soften the glycolphthalate mounting cement).

Surface treatments that resulted in shallow, angled depressions; chemical etching without pretreatment; and thin, sintered glass frit layers all had the same absence of active nucleation sites. Typical surfaces of this type are shown in Fig. 2. The morphology of these surfaces is best shown in the oblique SEM views.

3.2. *Group II – partially nucleating surfaces*

The surfaces in this group show an intermediate

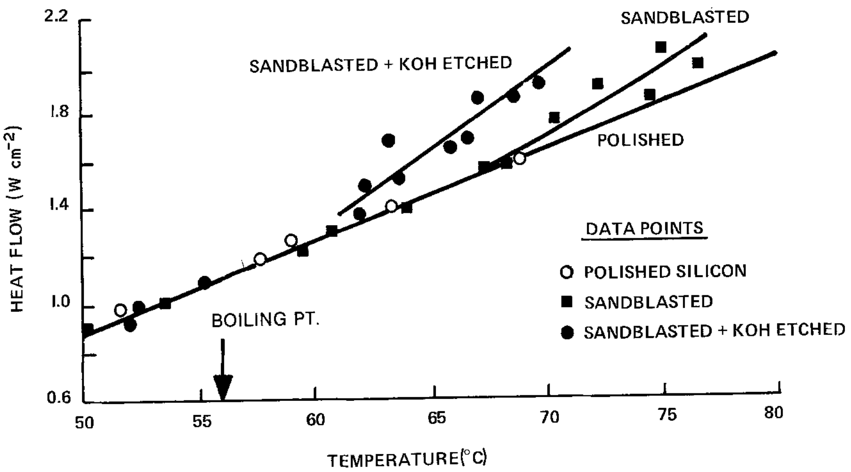

Fig. 9. Heat transfer of Si to C_6F_{14} for bare, sandblasted, and sandblasted and etched surfaces.

behaviour. There are some nucleation sites apparent on the wafer; their distribution is irregular, and small changes in treatment lead to large changes in performance. Boiling commences between 1.4 and 1.8 W cm^{-2}. Examples in this group include the sandblasted surfaces of Fig. 1. The surfaces are much rougher than the non-nucleating surfaces, with some fairly deep pits. The sandblasted plus pyrocatechol etched surface, Fig. 5, was the best of the partially nucleating group, with the surface appearing as an array of shallow pyramids.

3.3. *Group III – fully nucleating surfaces*

These surfaces exhibit the best boiling behaviour that we have seen for the silicon–perfluorohexane system. Boiling can be initiated below 1 W cm^{-2}. Typical surfaces, such as the sandblasted and KOH-etched sample of Fig. 4, are highly complex, with long re-entrant cavities. The same kind of complexity is evident in the etched gold–silicon surface of Fig. 7, which appears to be a series of rectangular projections approximately perpendicular to the bulk silicon. Another surface that showed full nucleation capability, and the lowest boiling initiation point, was a heavy layer of sintered glass. This surface was complex, containing many irregular projections and very deep cavities. It succeeded in providing full nucleation without the necessity of damaging the surface (as in the etching processes). The anodically etched [3] (porous silicon) surface performed well, but erratically. On some portions of the surface, boiling was initiated at power levels under 1 W cm^{-2} and proceeded actively at higher power levels, whereas in adjacent regions (dimension of the order of cm), no boiling was noted.

The heat transfer curve in Fig. 9 shows the heat flow as a function of temperature for conventionally polished silicon surfaces, sandblasted as well as sandblasted plus KOH-etched surfaces. The onset of boiling is indicated by the departure of the curve from the linear convection relationship of the polished silicon surface. At any power level above the onset of boiling, the surface temperature of the boiling surface is lower than that of the non-boiling surface.

4. Conclusions

The present work demonstrates that:

(1) a conventionally polished Si surface does not satisfactorily initiate nucleate boiling in perfluorohexane at heat flow levels below 2.4 W cm^{-2};

(2) satisfactory nucleation was achieved by all of the following classes of surface treatments at heat flow levels below 1.0 W cm^{-2}: (a) introducing lattice defects into the silicon, followed by a chemical etch; (b) forming a solid eutectic layer on the silicon surface, followed by the removal of one of the phases; (c) depositing an inert porous layer on the silicon.

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