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The effects of processing conditions on the density and microstructure of hot-pressed silicon powder

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Silicon powder was hot pressed into polycrystalline wafers 1.5 in (~ 3.8 cm) diameter using various processing conditions. The submicrometre powder used was a by-product of the fluidized bed decomposition process of silane (SiH_4) in the production of silicon pellets. The effect of temperature (1250–1300 °C), pressure (2000–3000 p.s.i.; 13.18–20.67 N mm^{-2}) and ambient (argon, hydrogen, vacuum) on the density of the hot-pressed powder was studied. All wafers processed had densities $> 92\%$ of the theoretical density of silicon as determined by Archimedes' density measurements. Hydrogen was found to increase the densification rate of powdered silicon. The mechanism by which this occurs is believed to be the reduction of the native oxide layer of the powders resulting in increased surface transport. The microstructure of the polycrystalline wafers was examined by scanning electron microscopy, and transmission electron microscopy. The general microstructure of the polycrystalline wafers consisted of micrometre-sized grains with twins, stacking faults, and dislocations within the grains. However, under hot-pressing conditions of 1300 °C, 2000 p.s.i., and a hydrogen ambient, the grains of the wafer were on the order of 1 mm. The silicon wafers contained iron, aluminium, carbon and oxygen impurities as determined by secondary ion mass spectroscopy.

1. Introduction

In the sintering process, the driving force for densification is the free energy decrease associated with the decrease in surface area of the particles [1]. The addition of an applied uniaxial pressure in the hot-pressing process provides an increased driving force for the consolidation of powders. Factors of importance in hot pressing are time, temperature, particle size and geometry, pressure, processing atmosphere, and activation energy for atom diffusion [2].

In general, the first step in hot pressing involves the cold compaction of the powder to about 60%–70% theoretical density (TD) by application of pressure which promotes sliding and rearrangement of the powders. Also during compaction, plastic flow occurs at the grain contacts and the extent of the flow is dependent on the ratio of applied stress in the die to the stress at the particle contact points [3]. Finally, densification occurs by pressure-directed diffusion. The densification rate during hot pressing is greater than pressureless sintering by a factor essentially proportional to $L/(R\gamma)$ where L is the applied load, R is the grain radius, and γ is the surface energy [3].

Covalent materials like silicon are sinterable but complete densification is difficult to achieve [4]. Parameters that limit the densification of silicon include slow self-diffusion and grain-boundary diffusion, which are essential for shrinkage [5]. Additionally, a native oxide layer (3–5 nm) on the silicon powders is believed to slow the densification. The exact nature of this phenomenon is not fully understood; however, it has been suggested that the thin oxide layers inhibit surface diffusion [5] and allow competing densification mechanisms to dominate the sintering of ultrafine silicon compacts [6]. It is therefore believed that the removal of this oxide layer will lead to an increased densification rate of silicon powders.

The present effort had two principal objectives. First, the hot-pressing conditions required to produce a polycrystalline silicon wafer with a density approaching the theoretical density of silicon were to be identified. Second, the microstructures of the hot-pressed wafers were to be analysed and correlated to the conditions employed during hot pressing.

2. Experimental procedure

The polycrystalline silicon powder used was supplied by Ethyl Corporation. The powder is a by-product of the fluidized bed decomposition process of silane for the production of silicon pellets (1–3 mm diameter). The average particle size of the powder was ≈ 0.26 μm, and had a particle size range of 0.05–3 μm as determined by particle-size measurements performed on a Horiba particle-size analyser. In addition, the powder contained a small amount of polycrystalline silicon pellets (≈ 10 vol %) intermixed in the powder. The as-received powder was hot pressed using

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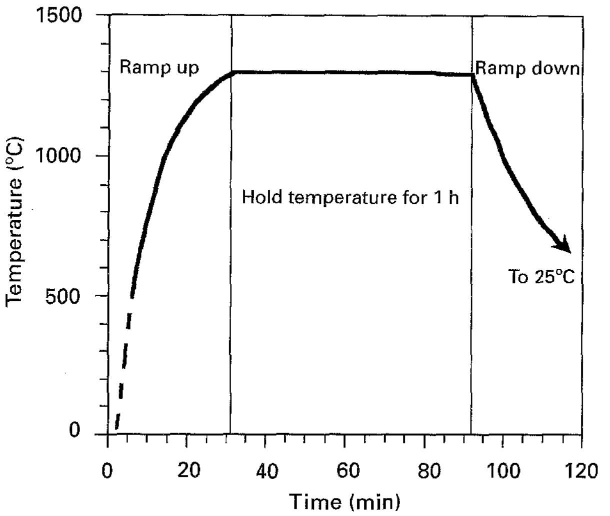

Figure 1 Typical temperature profile for a hot-pressing run (at 1300 °C).

a Centorr hot press (Model HP-4 × 5) equipped with a 1.5 in (~3.8 cm) inner diameter graphite die and punch set lined with grafoil (graphite foil). The grafoil was used to isolate the powder from the graphite die to prevent a possible reaction which, in turn, would make it difficult to remove the hot-pressed wafer from the die. The silicon powder was exposed to air prior to hot pressing. Therefore, a large oxygen concentration was expected due to native surface oxide layers on the powders.

In the hot-pressing system, the load was applied to the top punch impacting the silicon powder, while the bottom of the assembly was stationary. Force was applied by the downward movement of the top plunger through a hydraulic hand pump. Movement of the top plunger of the hot press was monitored during the runs using a micrometer. R.f. coils were used to heat the assembly. Samples were pressed at pressures of 2000 and 3000 p.s.i. (13.78 and 20.67 $\mathrm{N\,mm^{-3}}$) and were held at temperatures of 1250 and 1300 °C for 1 h in either a vacuum (10^{-1} torr; 1 torr = 133.322 Pa), an argon overpressure, or a 2.0% H/Ar balance overpressure. A pyrometer was used to monitor the temperature of the sample within an accuracy of ± 50 °C. A typical temperature profile for a hot-pressing run is shown in Fig. 1.

Bulk densities were measured according to ASTM 373-72. Sample preparation for the density measurements included quartering of the silicon wafers and grinding of all sides of the quarter pieces to remove both residual grafoil and a thin SiC layer that had resulted from the reaction between the silicon and the grafoil. The microstructures of the hot-pressed wafers were examined using a Jeol JSM-6400 scanning electron microscope (SEM) and a Jeol 200CX transmission electron microscope (TEM). Samples for the SEM were polished and etched in a SIRTL etch [7] to reveal the grain boundaries. For TEM, the samples were first polished down to a thickness of ≈50 μm using 5 μm Al_2O_3 powder and then argon-ion milled to electron transparency. The impurities in the hot-pressed wafers were analysed by secondary ion mass spectroscopy (SIMS) on a Cameca IMS-4f double focusing, magnetic sector ion microanalyser (Charles Evans West). Oxygen-ion bombardment was used to detect aluminium and iron, and caesium ions were used to measure oxygen and carbon contents. Ion-implanted float-zone silicon wafers were used as standards.

3. Results and discussion

3.1. Processing conditions

Temperature, pressure, and ambient were varied to study their effect on the density and microstructure of hot-pressed silicon. In general, each processing condition that was varied had an effect on the density of the hot-pressed wafers. However, the microstructures of the wafers were indistinguishable with the exception of the wafers processed in hydrogen at 1300 °C, as will be discussed in the following sections. Parameters that remained constant in the study were processing time (1 h + ramp), and silicon particle size and geometry. Mechanisms for densification of the silicon powders will be discussed below. Among these mechanisms we include surface diffusion which has an associated activation energy. This transport process, however, can be hindered by the presence of a surface oxide [5]. Therefore, the removal of this possible hindrance to the densification process by the variation of some processing condition is of importance, as it may lead to a difference in wafer density and/or microstructure.

3.2. Density measurements

All of the wafers had densities > 92% TD as shown in Fig. 2. The densities of the samples generally increased for both increases in pressure and in temperature. These results compare well with those published by Wang *et al.* [8] and can be explained by the fact that the driving force increases with increasing temperature and applied pressure. However, the density appears to be affected more by changes in temperature than by changes in pressure. The data also suggest that a reducing atmosphere of 2.0% H/Ar balance improves the densification of the silicon powder. The samples pressed in the hydrogen ambient had higher densities than those processed in argon or vacuum

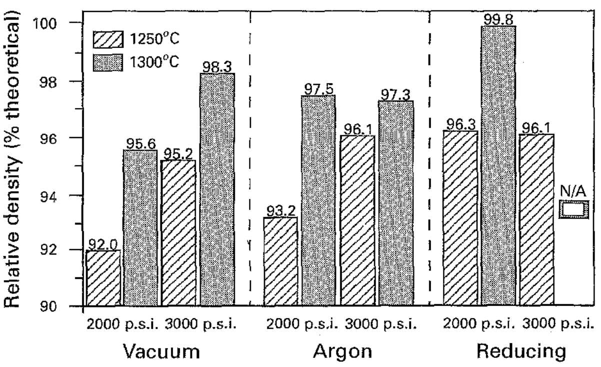

Figure 2 Bar chart representation of the density data. N/A = not available. 10^3 p.s.i. = 6.89 $\mathrm{N\,mm^{-2}}$.

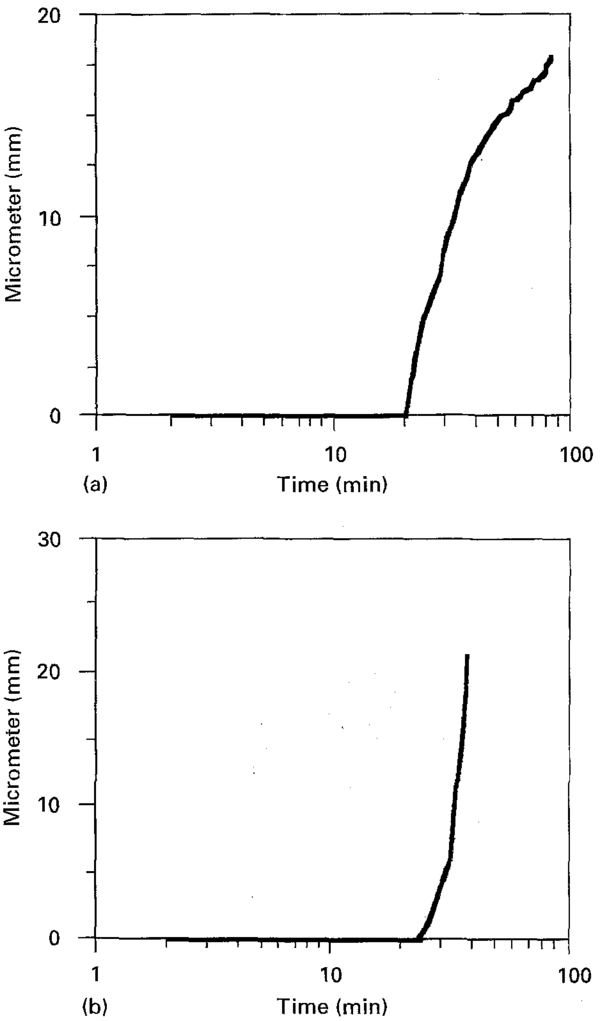

Figure 3 Micrometer versus log time plot: (a) typical run, (b) reducing atmosphere, 1300 °C, 2000 p.s.i.

atmospheres. The role of hydrogen is believed to be one that increases the rate of reduction of the native oxide layer of the powders leading to an increase in the rate of densification possibly by increasing surface transport. There appeared to be no difference between the argon and low-vacuum ambients on the hot-pressing behaviour of the silicon.

The downward movement of the top plunger during hot pressing was indicative of the increasing density of the sample and was monitored throughout the runs using a micrometer. Densification of the powder, past its cold-compacted state, typically began about 20 min into the hot-pressing run or at around 1200 °C. A semilogarithmic plot of a typical run for micrometer movement as a function of time is shown in Fig. 3a. The data show an approximately proportional increase in density as a function of time. Observations of proportionality between the density of hot-pressed samples and the logarithm of process time is common and is termed the semilogarithmic law [9]. This behaviour has been explained by mechanisms relating to grain growth and to dislocation creep [9]. The observation of the law itself, however, cannot be taken as a sufficient indication of a particular densification mechanism but does provide the means of a workable model for the interpretation of the hot-pressing kinetics. In the case of hot-pressed silicon, however, the proportionality is not direct, as shown, which leads to further ambiguity of the densification mechanism(s).

The hot-pressed silicon samples pressed in a reducing hydrogen atmosphere at 1250 °C showed little difference in densification behaviour and microstructure when compared to wafers processed in vacuum and argon. However, it was found that samples processed in a reducing atmosphere at 1300 °C behaved quite differently from the rest of the samples. Micrometer movement became very pronounced after only a few minutes at the holding temperature for these samples (Fig. 3b). A sample pressed at 3000 p.s.i. (20.67 N mm^{-3}) was found to have been completely squeezed through the sides of the die and lost, while a sample pressed at 2000 p.s.i. (13.78 N mm^{-2}) was pressed for only 10 min before the hot-pressing system was shut down owing to the rapid micrometer movement. The latter sample was characterized. This behaviour was not observed in hot-pressing runs processed at 1300 °C in vacuum or in an argon ambient. It is therefore believed that the hydrogen is influencing the densification behaviour of the silicon powder, possibly by removal of the thin native oxide layers on the powders by the following reaction [10]

$$2H_2 + SiO_2 \rightarrow 2H_2O + Si \qquad (1)$$

Hydrogen is often used to reduce the silicon powder–oxide layer during nitridation. The nitridation of silicon is typically carried out in the presence of hydrogen to increase the reaction rate [11]. Although the exact role of hydrogen in the nitridation process is unclear, it is well established in the literature that small additions of hydrogen to the nitriding gas greatly enhance the nitridation kinetics. Hydrogen is believed to promote the removal of the native oxide and prevents the oxygen from reoxidizing the silicon [11]. The partial pressure of oxygen during the nitridation process is observed to diminish considerably in the presence of hydrogen at temperatures exceeding 1300 °C [11]. Hydrogen reacts with the oxygen and prevents it from recombining with the exposed silicon surface, thus allowing the nitridation reaction to be greatly enhanced at lower temperatures [11]. It can be expected that hydrogen will affect the hot pressing of silicon powders in a similar manner.

Commonly reported mechanisms for densification in hot pressing include diffusional creep (bulk, grain boundary, surface) [12], dislocation creep (plastic flow) [8], grain-boundary and particle fragmentation [13]. Wang *et al.* [8] hot-pressed silicon powders in vacuum (10^{-5} torr; 1 torr = 133.322 Pa) for various times and achieved densities that ranged from ≈80%–98% TD. The reported mechanism for densification of the silicon powders was dislocation creep as determined by construction of a deformation map for silicon. This mechanism was believed to dominate over diffusional creep, primarily because of the low volume diffusion coefficient for silicon. Möller and Welsch [5] studied the sintering of silicon and determined that bulk diffusion was the dominant mechanism for silicon densification. Grain-boundary diffusion was also recognized as a possible mechanism but was believed to be hindered by the presence of the oxide films. On the other hand, Coblenz [6] reported that surface diffusion is the dominant mass-transport path for sintered silicon but is often inhibited by oxygen, thereby allowing shrinkage to occur by either grain-boundary or bulk diffusion.

In the case of hot-pressed silicon, it is possible that all of the mechanisms so far considered, as well as others not yet discovered, contribute to some extent toward final densification during the entire hot-pressing process. Any one mechanism may be a major contributor at a particular time, but is aided by the others. From the results of this experiment, it is apparent that the use of hydrogen as an ambient in the hot pressing of silicon powders influences the densification mechanism(s). The mechanisms most effected by hydrogen would include surface and grain-boundary diffusion.

3.3. Microstructure

The microstructure of the hot-pressed wafers was analysed by SEM and TEM. The grains in the hot-pressed silicon were clearly visible under the SEM after exposure of the samples to the SIRTL etch (see Fig. 4a and b). Limited grain growth appears to have occurred in the hot-pressed wafers as the grain size of the wafers is larger than the average grain size of the as-received polycrystalline powder (submicrometre). The calculated grain sizes of the compacts are shown in Table II and were calculated using the following equation [14]

$$d = 1.5 \times l/(n \times m) \qquad (2)$$

where l is the line length of the micrograph, m is the micrograph magnification, n is the number of grains crossed by the line, and 1.5, a parameter assuming spherical grains. An average grain size for each sample was obtained by calculating the grain size using data from three separate measurements across the micrograph.

The pores existing in the low-density samples had jagged shapes and were nearly continuous around the individual multicrystalline particles. These pores were clearly in the earlier stages of densification, because in the wafers processed under conditions giving rise to increased density, the pores were found to be more rounded and isolated from one another. Bonding between the multicrystalline particles appeared to be continuous with no distinct interface at the connection points.

Transmission electron microscopy was used to reveal the defects in the fine-grained hot-pressed wafers. There were no obvious microstructural differences between samples pressed in vacuum, argon, or hydrogen (at 1250 °C). The microstructures of the wafers consisted of micrometre-sized grains containing dislocations, stacking faults and twins (Fig. 5a). Möller and Welsch [5] noted similar microstructures for sintered silicon powder and found that further annealing of the compacts (1 h at 1350 °C) did not produce any significant changes in the microstructure. They had expected that recrystallization and growth of large grains would occur at higher temperatures but instead saw only a reduction in the twin density. In addition, no amorphous particles were found in the hot-pressed wafers.

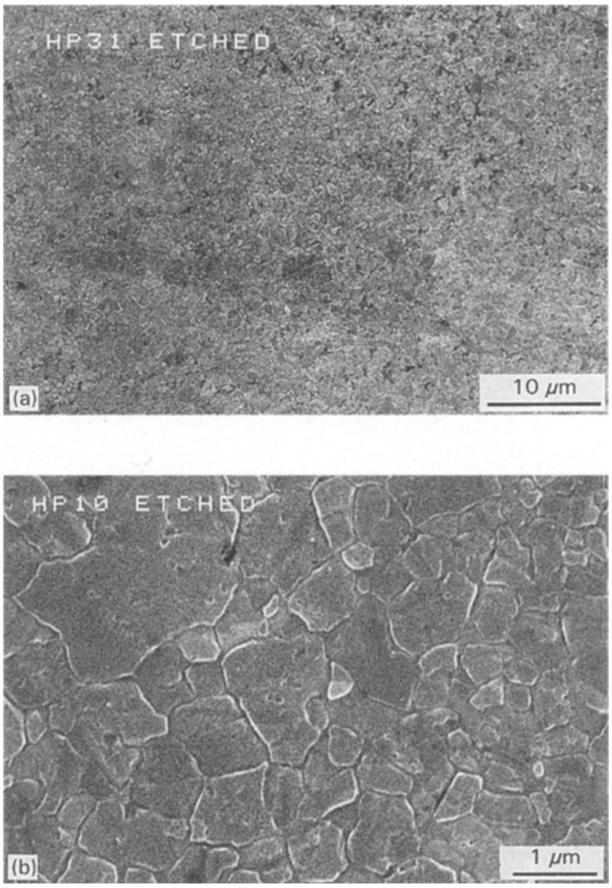

Figure 4 Scanning electron micrographs of wafer microstructure for samples pressed under conditions of (a) 1250 °C, 3000 p.s.i., vacuum, at × 2000, and (b) 1300 °C, 2000 p.s.i., argon at × 15 000.

TABLE I Average wafer grain size (10^3 p.s.i. = 6.89 N mm^{-2})

Atmosphere	Pressure (10^3 p.s.i.)	Grain size (μm)	
		1250 °C	1300 °C
Vacuum	2	0.769	1.24
	3	1.24	1.32
Argon	2	0.872	1.07
	3	0.86	1.12
Reducing	2	1.11	1×10^3
	3	1.11	N/A

TABLE II SIMS analysis of carbon and oxygen in hot-pressed wafers processed in three different ambients as referenced to the background concentrations in ion-implanted float-zone wafers

Impurity	Concentration (at cm^{-3})			
	Float zone	Vacuum	Argon	Hydrogen
O	2×10^{16}	1.5×10^{21}	1.5×10^{21}	1×10^{20}
C	9×10^{16}	8×10^{20}	2.5×10^{20}	1×10^{19}

The microstructure of the sample pressed in hydrogen at 1300 °C is much different than the microstructures found in the other hot-pressed samples (Fig. 5b). This difference is believed to be due to the

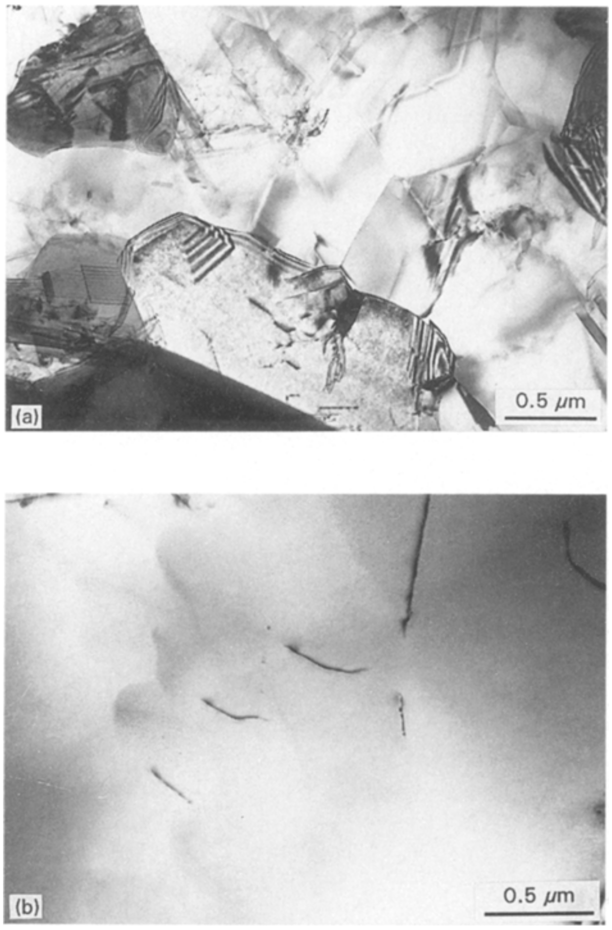

Figure 5 TEM bright-field micrographs of hot-pressed wafers: (a) 1250 °C, 2000 p.s.i., vacuum, at × 30 000; (b) 1300 °C, 2000 p.s.i., 2% H, at × 30 000.

combination of temperature and atmosphere effects. As shown in Fig. 3b, the top plunger movement versus time plot displays a change in slope at approximately 32 min into the run. It is believed that at this point the oxide layer is completely removed by the reducing atmosphere or that the inhibiting characteristics of the oxide have diminished and are overcome by the driving force for densification and grain growth.

It is possible that the silicon powder melted under these conditions. As previously stated, the pyrometer used had an error of ± 50 °C as stated by the manufacturer. However, temperature measurements using two different thermocouples showed that the temperature could be as much as a hundred degrees off, especially at higher temperatures. In addition, the microstructure observed in this sample was comparable to the microstructure observed in a sample of silicon powder that was intentionally melted in the hot press without application of pressure (1410 °C).

3.4. SIMS results

Secondary ion mass spectroscopy measurements were run to measure the amounts of iron, aluminium, carbon and oxygen in the fine-grained matrix of the wafers. A chemical analysis of the starting powder as provided by Ethyl Corporation is as follows: transition metals < 2 p.p.m. atomic; carbon < 4 p.p.m. atomic; oxygen < 2000 p.p.m. atomic. The wafers used in the SIMS experiments were chosen to compare the effects of processing on the purity of the samples. Wafers examined were processed in the hot press at 1250 °C and 3000 p.s.i. (20.67 $\mathrm{N\,mm^{-2}}$) under different ambients. Because of the small grain size, there could be no distinction made between impurities residing at the grain boundaries and those within the grain. Measurements were taken after sputtering 1 μm into the wafer to eliminate surface contaminant effects. The results of the analysis are summarized in Table II.

As expected, oxygen was found to be very abundant in the hot-pressed wafers. This high oxygen concentration is attributed to the native oxide layers of the silicon powders prior to processing. It is to be noted, however, that the concentration of oxygen in the hydrogen-pressed wafer is an order of magnitude lower than in wafers processed in either vacuum or argon ambient. The high carbon concentration of the hot-pressed wafers can be attributed to the use of graphite dies and grafoil. The silicon powder was in direct contact with the grafoil thus providing a source of carbon. Owing to the numerous grain boundaries in the hot-pressed wafers, impurities could penetrate deep into the wafers via grain-boundary diffusion. The effect of carbon on the densification of silicon is not clear; however, its effect is expected to be minimal [5]. Aluminium and iron were scanned for because they were known impurities in the grafoil. SIMS analysis revealed both aluminium and iron to exist in concentrations of $3 \times 10^{16}\,\mathrm{at\,cm^{-3}}$ (i.e. < 2 p.p.m.). Thus, there appears to be no appreciable increase in aluminium and iron in the wafers as a result of processing as compared to the starting powder concentrations.

4. Conclusions

Polycrystalline silicon wafers have been processed using a hot press and waste silicon powder. The density of the 1.5 in (~ 3.8 cm) diameter wafers exceeded 92% TD with the highest density wafers being processed in a hydrogen ambient. Oxygen is believed to inhibit both surface and grain-boundary diffusion leading to a decrease in densification of the silicon powder. Hydrogen appears to play a role in the densification of the silicon powder, possibly by removing the native oxide layer on the silicon particles leading to increased surface and/or grain-boundary transport. In general, the microstructure of the wafers consisted of defective micrometre-sized grains as revealed in TEM and SEM. The wafers contained iron, aluminium, carbon and oxygen as detected by SIMS.

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