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Grain growth and mechanical properties in bulk polycrystalline silicon

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The grain structure of bulk polycrystalline silicon has been examined as a function of annealing temperatures and times between 1000 and 1400°C and 6 to 24 hours, respectively. The initial high aspect grain structure decomposes into roughly equiaxed grains at 1000°C over the course of 24 hours. The grains proceed to grow via Oswald ripening with an activation energy for grain growth of 1.49 eV. The hardness increases slightly during annealing and the subsequent transformation to an equiaxed grain structure, from a Vickers hardness of 964 to 1160 kg/mm^2. The fracture toughness is 0.8 MPa(m)$^{1/2}$ in the as grown structure, and increases to 1 MPa(m)$^{1/2}$ in annealed samples. The hardness and fracture toughness are independent of grain size for grain diameters between 2.7 and 4 μm. © *2001 Kluwer Academic Publishers*

1. Introduction

Polycrystalline silicon is the raw material used in the production of single crystal silicon, whether grown from Czochralski or float zone methods [1]. This material is produced by chemical vapor deposition (CVD) as described in more detail by McCormik [2]. The resulting polycrystalline product is used either in the as grown form in float zone processing or is broken into smaller pieces for loading into Czochralski growth furnaces. In either case, the mechanical properties of the material play an important role; in the first case fracture in the rods is detrimental whereas in the second fracture is required for further processing.

Much of the literature on grain growth in polycrystalline silicon focuses on thin films grown via CVD [3–10]. These results, which document the effects of impurities as well as the various microstructures which occur in these films, are instructive as to the possible ranges and rates of growth in the corresponding bulk materials. Activation energies for grain growth have been calculated by several researchers, ranging between 0.8 eV [10] and 2.4 eV [3, 4, 8, 9]. It has been noted in some of these cases that there is a transition between primary and secondary recrystalization as the structure of the grains change from very fine grains (sub μm) to larger (1–2 μm), and activation energies have been observed for the secondary recrystalization between 1 eV [3] and 3.8 eV [6]. However, as surface energy can play a role in the growth of these thin films, which can lead to a larger activation energy for diffusion across grain boundaries, [6] it is possible that the bulk grains may not grow either at the same rate or via the same mechanism. Additionally, the bulk microstructure may have little resemblance to that grown in thin film form, as the initial growth of the bulk crystals occurs on crystalline, rather than amorphous, silicon. Therefore, this study was performed to examine the relationships between microstructure and the resulting properties after various annealing treatments in high purity bulk polycrystalline silicon.

2. Experimental procedure

The microstructure of polycrystalline silicon grown via a chemical vapor deposition process [2] was characterized using visible light and scanning electron microscopy (SEM). All samples were etched using a 4 : 1 ratio of HNO_3 to HF for 3–5 minutes, rinsed in deionized water, etched for another 2 minutes, and then rinsed again in deionized water. Grain sizes were measured using the Heyn intercept method with a circular line in an attempt to average the grain size of non-equiaxed structures. [11] Impurities in these samples were below 50 atomic parts per trillion for boron, below 250 atomic parts per trillion for phosphorus, and below 500 atomic parts per billion for carbon.

Samples were cut from the polycrystalline rod equidistant from the center of the rod to account for non-uniform grain structures, the average grain size increases as the distance from the center to the edge of the rod increases. These samples were encapsulated in quartz ampoules, evacuated to pressures of $\approx 10^{-5}$ torr, and then heat treated. Samples were heated and cooled at a rate of 2°C/min., and held at the soak temperature for either 6, 12, or 24 hours.

After the various heat treatments, the samples were removed from the encapsulation, mounted and polished using standard metallographic techniques. The hardness was measured using a LECO MVK-G3 Vickers Microhardness Tester. Loads between 25 and 2000 g

were applied to a Vickers tip; the largest loads generate large fracture regions and therefore the lighter loads were used to determine the hardness of the samples. Fracture toughness was estimated using the indentation fracture method detailed by other researchers [12, 13]. Cracks emanating from the indentation were measured using either SEM or visible light microscopy.

3. Results and discussion

3.1. Grain growth kinetics

The microstructure of the as received polycrystalline silicon is shown in Fig. 1. The material consists of numerous slender, closely arranged parallel grains forming a vane on either side of a central shaft, with the individual "feather" vanes being approximately 1–2 μm in diameter and approximately 10 μm long. Fig. 2 shows the grain structure of the samples heat treated for 12 hours at 1375°C. There is a clear change between the "feather" like structure in Fig. 1 to the relatively equiaxed morphology in Fig. 2. Fig. 3 shows the transition between these two structures; this sample, heated at 1200°C for 12 hours, exhibits remnants of the highly directional structures but consists primarily of equiaxed grains. The grain size as a function of annealing temperature and time is shown in Table I. Even after 24 hours at 1375°C no evidence

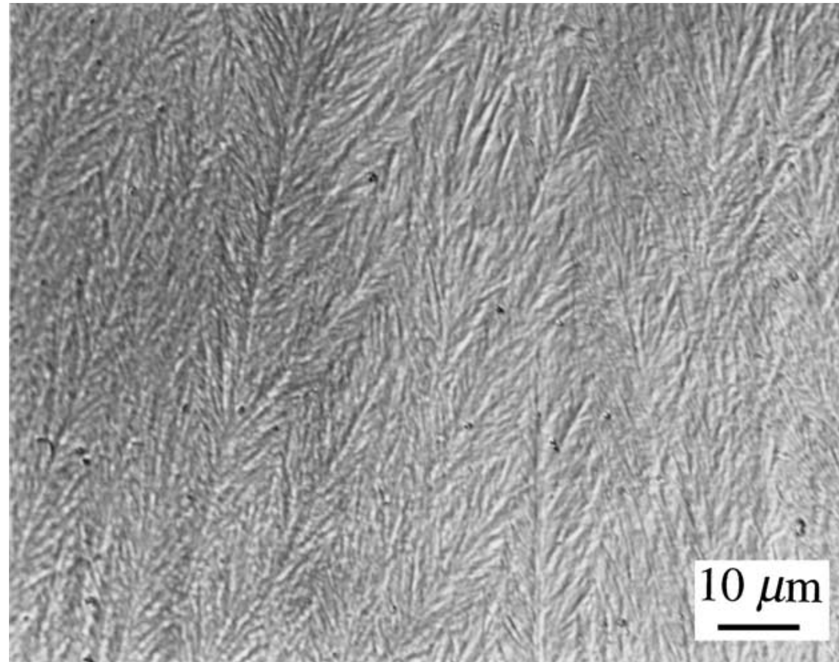

Figure 1 Optical micrograph showing grain structure of as grown polycrystalline silicon. Note the highly textured microstructure.

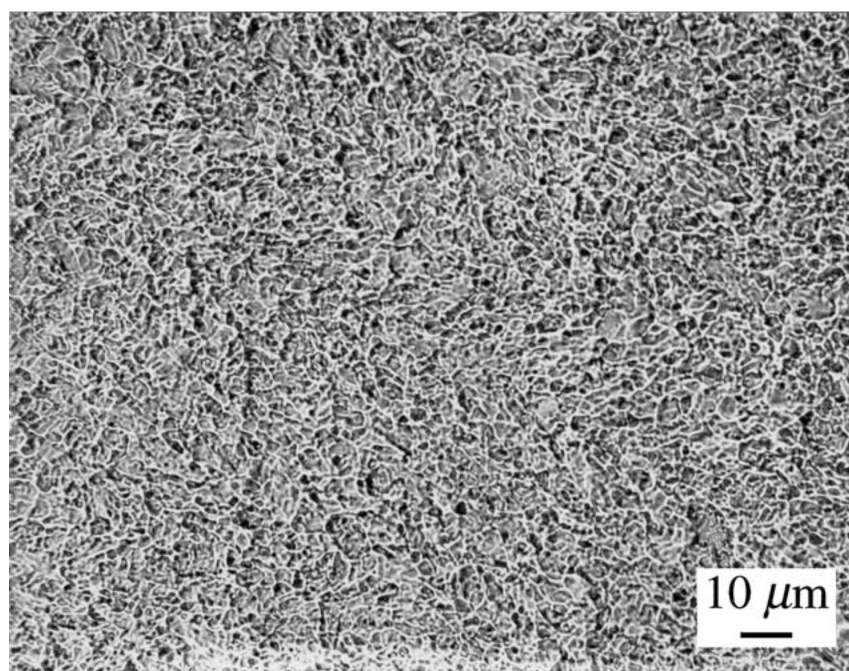

Figure 2 Grain structure of polysilicon after being heat treated for 12 hours at 1375°C. Equiaxed grains have formed and there is no clear evidence of the original microstructure.

TABLE I Average grain size, hardness and fracture toughness of annealed polycrystalline silicon

Annealing temperature (°C)	6 hours: Average grain diameter, μm	6 hours: Vickers hardness kg/mm^2	6 hours: K_{Ic} MPa(m)$^{1/2}$	12 hours: Average grain diameter, μm	12 hours: Vickers hardness kg/mm^2	12 hours: K_{Ic} MPa(m)$^{1/2}$	24 hours: Average grain diameter, μm	24 hours: Vickers hardness (kg/mm^2)	24 hours: K_{Ic} MPa(m)$^{1/2}$
1000	2.95	1221 ± 98	0.93 ± 0.21	2.86	1335 ± 256	1.03 ± 0.3	2.69	1139 ± 103	0.96 ± 0.2
1150		–	–	2.95	1284 ± 120	0.97 ± 0.34		–	–
1200		–	–	3.08	1140 ± 342	0.57 ± 0.36		–	–
1250	2.99	1023 ± 259	1.52 ± 0.38	3.15	990 ± 335	1.0 ± 0.23	3.15	1229 ± 135	1.11 ± 0.12
1300	3.07	1196 ± 616	1.47 ± 0.70	3.35	1055 ± 71	1.3 ± 0.18	3.39	1182 ± 126	0.81 ± 0.22
1350	3.31	1131 ± 173	0.99 ± 0.59	3.68	1083 ± 114	1.13 ± 0.17	3.62	1245 ± 163	0.85 ± 0.39
1375	3.43	1318 ± 141	0.94 ± 0.22	3.73	1022 ± 464	0.92 ± 0.09	3.76	1169 ± 84	1.05 ± 0.19
1400		–	–	3.99	1180 ± 200	0.77 ± 0.16		–	–

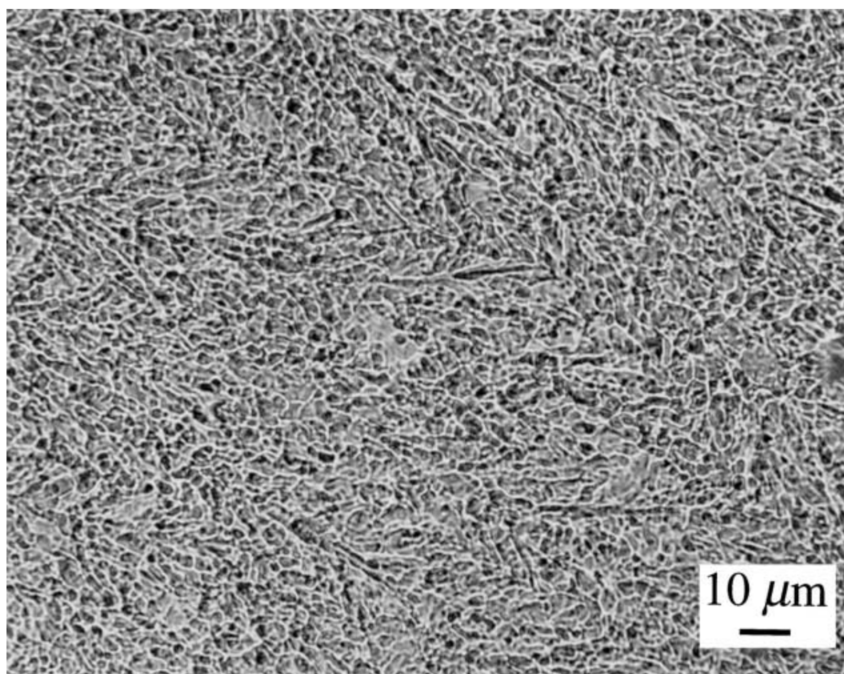

Figure 3 Polycrystaline silicon annealed at 1200°C for 12 hours. Remnants of the highly directional structures are present, but the sample consists primarily of equiaxed grains.

of abnormally large grains (indicative of secondary recrystalization) was found, as opposed to the behavior of polycrystalline silicon thin films [9].

The change from a high aspect ratio grain structure to relatively equiaxed grain structures suggests two basic steps must occur to account for the observed grain growth. First, the feather-like grain structure appears to decompose into sub-grains which are on the order of the smallest dimension of the high aspect grains. Similar phenomena have been observed in metallic systems, for instance tungsten grains with a 20 : 1 aspect ratio along the longitudinal axis of a highly drawn wire develop transverse grain boundaries upon annealing [14]. This transformation to equiaxed grains is the reason for the "inverted" grain sizes observed following the different heat treatments at 1000°C as shown in Table I. Since the transition at this temperature is not fully completed, the grain size determined from the Hyne intercept method is sensitive to the residual grain texture. Samples annealed for 6 hours at 1000°C had not recrystalized to the same extent as the sample annealed for 24 hours at this temperature. The resulting grain size is therefore larger, indicative of the presence of some of the longer original grains.

In the second step, the equiaxed grains proceed to grow and there is an increase in the average grain size. If it is assumed that the mean grain diameter, D, is proportional to the mean radius of curvature of the grain boundary, then the average velocity of the grain diameter, v, is given by [15]

$$v = \alpha M\, 2\gamma / D \tag{1}$$

where γ is the grain boundary energy, α is a proportionality constant on the order of unity, and M is the grain boundary mobility. The mobility can be expressed as [15]

$$M = \mu \frac{1}{T} \exp\left(-\frac{\Delta G^{a}}{kT}\right) \tag{2}$$

where T is the absolute temperature, k is the Boltzmann constant, ΔG^{a} is the activation energy for diffusion across a grain boundary. The final proportionality

constant, μ, is the available site jump frequency. By combining Equations 1 and 2, the grain boundary velocity is merely

$$v = \alpha\mu\frac{1}{T}\exp\left(-\frac{\Delta G^{a}}{kT}\right)\frac{2\gamma}{D} \cong \frac{dD}{dt} \quad (3)$$

which, when integrated with respect to time, t, and grain diameter allows the grain diameter to be expressed as a function of time as

$$D^2 = D_0^2 + \frac{C}{T}\exp\left(-\frac{\Delta G^{a}}{kT}\right)t \quad (4)$$

where D_0 is the initial grain size and $C = \alpha\mu\gamma$; effectively a constant in this equation.

By plotting the average grain diameter squared as a function of temperature, the three parameters can be determined using least square curve fitting routines. Specifically, D_0 was determined initially for all three samples, and then the average initial grain size was determined. This results in an average initial diameter of $\approx$2.7 μm, which is very similar to the grain size once the grains reach the equiaxed grain structure, and thereby helps support the method. Fixing D_0, the data were then fit for both C and ΔG^a for each time. The values of C ranged from 4.7×10^6 μm^{2}K/hr for the sample annealed for 24 hours to 4.1×10^7 μm^{2}K/hr for the sample annealed for 6 hours. The average value of C is 2.9×10^7 μm^{2}K/hr, which was then fixed and the curve fitting routine again applied to solve for ΔG^a. The final curve fit is shown in Fig. 4 along with the raw data for samples which consist primarily of equiaxed grains. The average activation energy for diffusion across the grain boundary is 1.49 eV.

An activation energy for grain growth of 1.49 eV corresponds roughly to one third the value of the activation energy of the self diffusion coefficient for single crystal silicon, 5.03 eV at temperatures above 1050°C [16]. This ratio is similar to that found when the activation

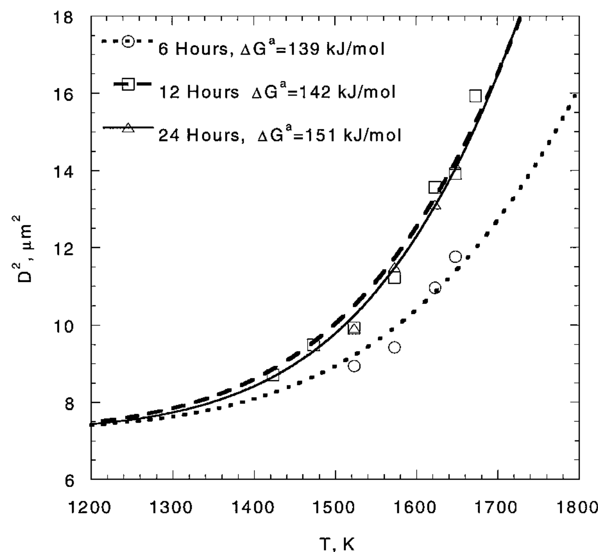

Figure 4 Relationship between average grain diameter and annealing temperature for all three times. The curve fit to Equation 4 is shown, along with the activation energy for diffusion across grain boundaries for all three times.

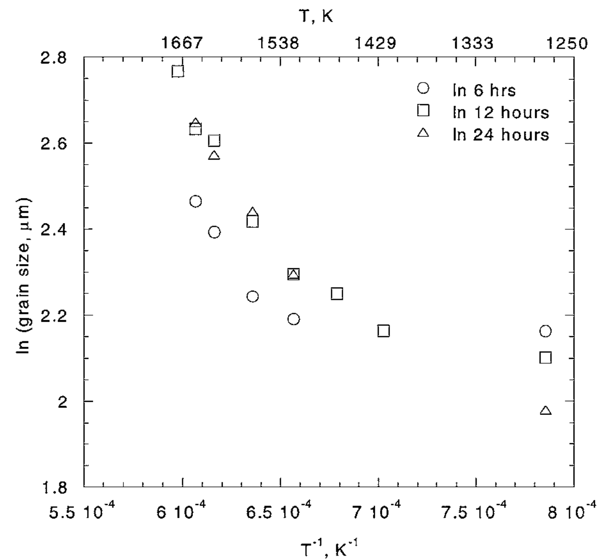

Figure 5 Relationship between ln (grain size) and inverse annealing temperature. The two energy controlled processes, transformation to equiaxed grain structure and the subsequent grain growth are represented by change in slope between 1300–1400 K.

energy for transfer across a grain boundary is compared to the activation energy for self diffusion in metals and ceramics [17]. In prior studies, researchers have identified activation energies for primary recrystalization ($\approx$1–2 eV) and secondary recrystalization and grain growth ($\approx$1–4 eV). The activation energy for grain growth in this study is on the order of the value determined for primary recrystalization in silicon thin films [3, 4, 8, 9].

Since the grains must first reach an equiaxed structure (recrystalize) before growth, and since there is basically an exponential dependence of grain size on temperature, it is instructive to examine these data in terms of logarithmic grain size versus inverse temperature, as shown in Fig. 5. The two step process is more evident using this scale; the lower temperature measurements clearly are not related to temperature changes in the same exponential relationship as the grain growth. Similar observations have been made in thin film grain growth [3, 5, 10], where at temperatures below 800–1000°C no or very little grain growth occurs. It should be noted that the C/T term in Equation 4 is not accounted for in Fig. 5, and therefore the deviation from linear behavior at the higher temperatures observed in Fig. 5 is expected.

3.2. Hardness and fracture toughness in annealed polycrystalline silicon

Hardness values taken at loads which did not generate large cracks for the as received sample are 964 ± 183 kg/mm^2. It should be noted that in all cases where loads above 25 g were applied to the sample, small radial cracks emanated from the corners of the indentation. Hardness numbers generated from such data can only be considered upper bounds, as will be discussed shortly. The fracture toughness was estimated by measuring the radial cracks generated at the corners of the Vickers indentation [12, 13] shown in Fig. 6. The fracture toughness of the as received sample was

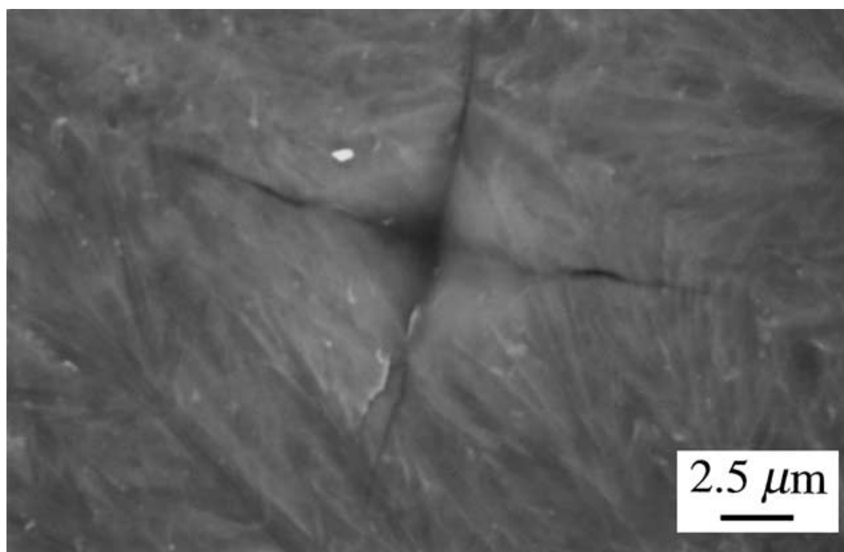

Figure 6 Vickers indentation with a 50 g load into as grown polysilicon. Cracks formed at the corners of the indentation are used to estimate fracture toughness.

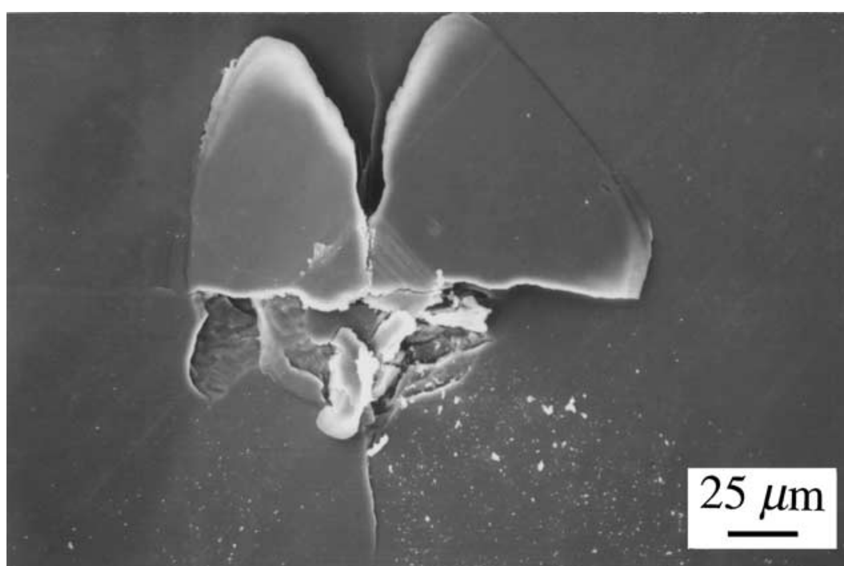

Figure 7 An indentation with a 200 g load into annealed polycrystalline silicon. Large lateral cracks and spalling are observed when indentations at this and higher loads are made in this material, and therefore are not used in the fracture toughness calculations.

0.81 $MPa(m)^{1/2}$. These measurements were made using primarily small loads (50–100 g) to minimize the amount of lateral cracking which leads to spalling at larger loads. A typical fracture morphology for loads above 200 g is shown in Fig. 7. The fracture toughness is given by

$$K_{IC} = \xi \left(\frac{E}{H}\right)^{0.5} \frac{P}{c^{1.5}} \tag{5}$$

where E is the Young's modulus ($\approx$180 GPa for polysilicon), H is the hardness or mean pressure of the indentation (note, this must be in GPa, not kg/mm^2), P is the indentation load, and c is the mean length of the radial cracks emanating from the corners of the Vickers impression. The parameter ξ ($=0.016 \pm 0.0004$) is a material-independent constant for Vickers-produced radial cracks [13]. The hardness and fracture toughness of the various samples is also shown in Table I. All hardness values reported in Table I are from low loads which either generate no cracks or radial cracks which are very small compared to the size of the indentation. The fracture toughness calculation uses the hardness from loads which did not generate cracks rather than the loads which caused the cracks, as H should be used as a measure of the resistance to plastic deformation in Equation 5.

As shown in Fig. 6, loads of 50 g and higher generated small radial cracks at the corners of Vickers indentations. The hardness values of the as received sample are at best upper bound estimates of the actual hardness. When cracking occurs around an indentation, energy which would produce deformation resulting in a larger impression instead goes into initiating and propagating cracks. As a result, a material which cracks during indentation will have a slightly smaller residual impression than an indentation into a material which does not crack during testing. This is the motivation behind determining a hardness value at loads which do not cause

cracks, and then using that value for subsequent fracture toughness calculations.

The hardness and toughness of most of the annealed samples were higher than the polycrystalline silicon tested in the as received state, with an average value of all the annealed samples of approximately 1160 ± 100 kg/mm^2. It is possible that this is due to a reduction in residual stresses in the material during annealing, but there is no direct evidence of that mechanism at this time. However, there is no consistent trend observed in the change in hardness and fracture toughness with annealing temperature and time. The hardness and fracture toughness appear to be basically independent of grain size over the range of grain sizes this study examined once the equiaxed grain structure has developed. Traditionally, it is assumed that harder materials are often more brittle, and a sample which has undergone grain growth would be softer than a similar material with a smaller grain size. The small change in average grain size over the course of this experiment makes it difficult to unequivocally state that these properties are independent of grain size. However, it should be noted that if a significant amount of deformation is accommodated by grain boundary sliding rather than dislocation motion in this rather brittle material, it is possible that this deformation mode could offset any possible Hall-Petch hardening which may occur.

4. Conclusions

The structure of polycrystalline silicon grown by chemical vapor deposition has been shown to change after annealing from an acicular grain structure to relatively equiaxed grains. This change in structure occurs over the course of approximately 24 hours at 1000°C. Average grain diameters range from 2.7 μm to approximately 4 μm after annealing for 24 hours at 1000°C and 1400°C respectively. Subsequent grain growth allows the determination of the activation energy for diffusion across grain boundaries, which is 1.49 eV. This value is similar to that reported in previous studies in thin films of polysilicon.

The Vickers hardness of the as grown structures is 964 kg/mm^2, and the average value raises slightly with annealing to 1160 kg/mm^2. The fracture toughness calculated from indentation induced cracking of the as grown sample is 0.8 MPa(m)$^{1/2}$, and increases slightly to 1.0 MPa(m)$^{1/2}$ following annealing. Almost all the annealing treatments appear to increase the hardness and toughness. Indentations greater than approximately 200 g cause massive lateral cracking leading to large regions of spalling around the indentation, therefore low loads must be used to measure the mechanical behavior of these materials with indentation methods.

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