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Deformation and recrystallization of polycrystalline silicon

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A systematic study of recrystallization of hot-deformed single and polycrystalline silicon has been carried out. New grains were formed by nucleation and growth at temperatures between 1280 and 1410° C and the final grain size was a function only of the degree of deformation. For polycrystalline chemical vapour deposition (CVD)-grown silicon hot-deformed at temperatures between 1100 and 1310° C it was established that the largest grains (of the order of a few millimetres) can be grown after about 5% deformation. At this low strain the rates of nucleation and growth were low and consequently the time needed to complete recrystallization was rather long (20 h). Below 4% deformation no recrystallization occurred (critical degree of deformation is 4%). For both single and polycrystalline silicon grain growth after primary recrystallization was limited. This was due to the low mobility of high-angle grain boundaries in covalently bonded materials.

1. Introduction

Polycrystalline silicon has become an important material for solar cell applications. Large areas of polycrystalline silicon can be grown relatively rapidly by the pyrolysis of SiH_4 or $SiHCl_3$ (chemical vapour deposition, CVD). A disadvantage of this material is that the grain size is only a few micrometres, whereas the grains must be at least $100\,\mu m$ to obtain a good efficiency for the solar cell. However, it is possible to increase the grain size of the as-grown layers by recrystallization, using the grown-in defects as a driving force (10^7 to 10^8 Pa) [1–3]. This process occurs at temperatures between 1250 and 1410° C (melting point) and is completed within a few minutes at 1380° C. The resulting grains are inhomogeneous in size. The original $\langle 110 \rangle$ fibre texture changes into a $\langle 111 \rangle$ fibre texture. Prolonged heating at high temperatures does not lead to significant grain coarsening as grain growth after primary recrystallization is extremely slow in this material.

A method which is generally used in metallurgy to induce recrystallization is plastic deformation. Hot-rolling of polysilicon may be a technique to induce growth of large grains upon subsequent annealing. This paper describes a systematic study of the influence of the degree of deformation, the deformation temperature, the strain rate and the annealing temperature on the final grain size of polysilicon.

2. Experimental details

Deformation experiments were carried out on bars of intrinsic CVD-grown polysilicon (high purity, semiconductor grade) obtained from Wacker-Chemitronic and Montedison, respectively. From these bars samples were diamond-core drilled, as indicated in Fig. 1. Samples A were used for uniaxial deformation in tension in a direction normal to the $\langle 110 \rangle$ growth direction, whereas Samples B were used for uniaxial compression in a direction parallel to this axis. Furthermore, compression experiments were done with Czochralski (Cz) grown $\langle 111 \rangle$ single crystals (high-ohmic) and with p-doped (1 to $10\,\Omega$cm) SILSO ingot polycrystals (Wacker-Chemitronic) with irregularly-shaped grains, 150 to $750\,\mu m$ in size, and no apparent preferred orientation. Before deformation all CVD-grown

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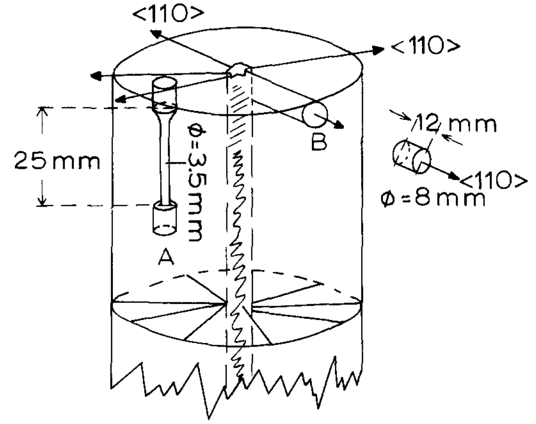

Figure 1 Orientations of samples cut from polycrystalline silicon bar (Wacker-Chemitronic).

samples were recrystallized at 1350° C since the as-grown material appeared to be extremely brittle. The deformation in tension was carried out with an Instron testing machine at 1140° C *in vacuo* at 10^{-3} mm Hg using strain rates between 3.3×10^{-4} and $3.3 \times 10^{-2}\ \text{sec}^{-1}$. Compression experiments were performed under flowing argon with a Hedeby testing machine at temperatures ranging from 1100 to 1310° C at a strain rate of 5×10^{-2} sec^{-1} using platens of Ta–10 wt% W. Series of samples were deformed in tension or compression between 2 and 60%. At the end of a test the load was removed and the samples were cooled to room temperature. Subsequent annealing was performed in gas-tight Al_2O_3 tubes under flowing argon.

3. Results

3.1. Samples deformed in tension

The cross-section of the deformed samples became elliptic with the larger diameter coinciding with the original ⟨1 1 1⟩ texture axis in the material. This anisotropy results from the non-random distribution of the {1 1 1} active glide planes due to the ⟨1 1 1⟩ fibre texture.

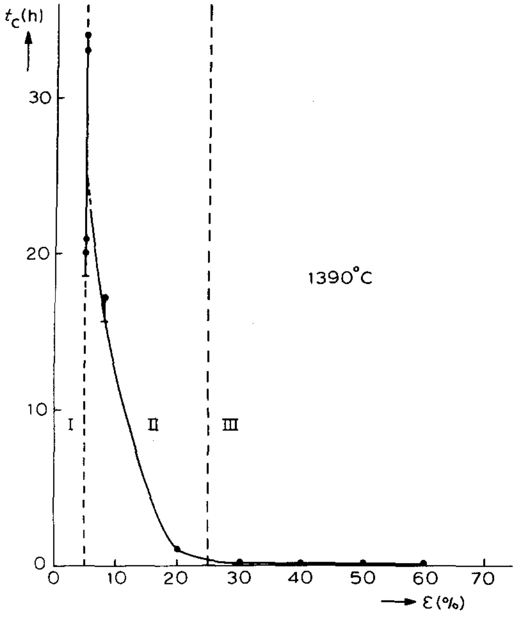

Figure 2 Time (t_c) needed for a complete recrystallization at 1390° C as a function of the degree of deformation.

All samples were studied in a plane normal to the tensile axis. Examination by optical microscopy showed that during deformation the dislocations had rearranged to a large extent into a cell structure. The dimensions of these cells were different for each deformed grain, varying from 1 to 30 μm in cross-section with an average value of 5 μm, independent of the value of the strain, ϵ. Upon annealing at temperatures between 1250 and 1410° C all samples deformed from 5 to 60% recrystallized by nucleation and growth. In Fig. 2 the time needed for a complete transformation (t_c) at 1390° C is plotted as a function of ϵ. For samples deformed between 25 and 60% (Region III) t_c was of the order of a few minutes only. This was also the case for as-grown (CVD) material. The resulting grain size was found to be nearly independent of ϵ. In Fig. 3a and b the structure after recrystallization of a 40% deformed sample and an as-grown sample are compared. After recrystallization of the as-grown material the grains were elongated along the ⟨1 1 1⟩ texture axis and inhomogeneous in size. In Fig. 4 a typical grain-size distribution is given for this kind of material. Although less pronounced, the grains after recrystallization of the 40% deformed sample were also more or less elongated along the original ⟨1 1 1⟩ texture axis. The corresponding grain-size distribution is shown in Fig. 5. In Fig. 6 the average values of the larger grain diameter determined in several areas of the surface of the samples are plotted as a function of ϵ. The volume-fraction recrystallized as a function of annealing time and temperature $X(t)$ is shown in Fig. 7 for $\epsilon = 40$ and 60%, respectively. The measured values of $X(t)$ were corrected for the times required to reach the annealing temperature. The volume-fraction of primary recrystallized material $X(t)$ can be described by [4]

$$X(t) = 1 - \exp[-\eta \pi N (vt)^3], \qquad (1)$$

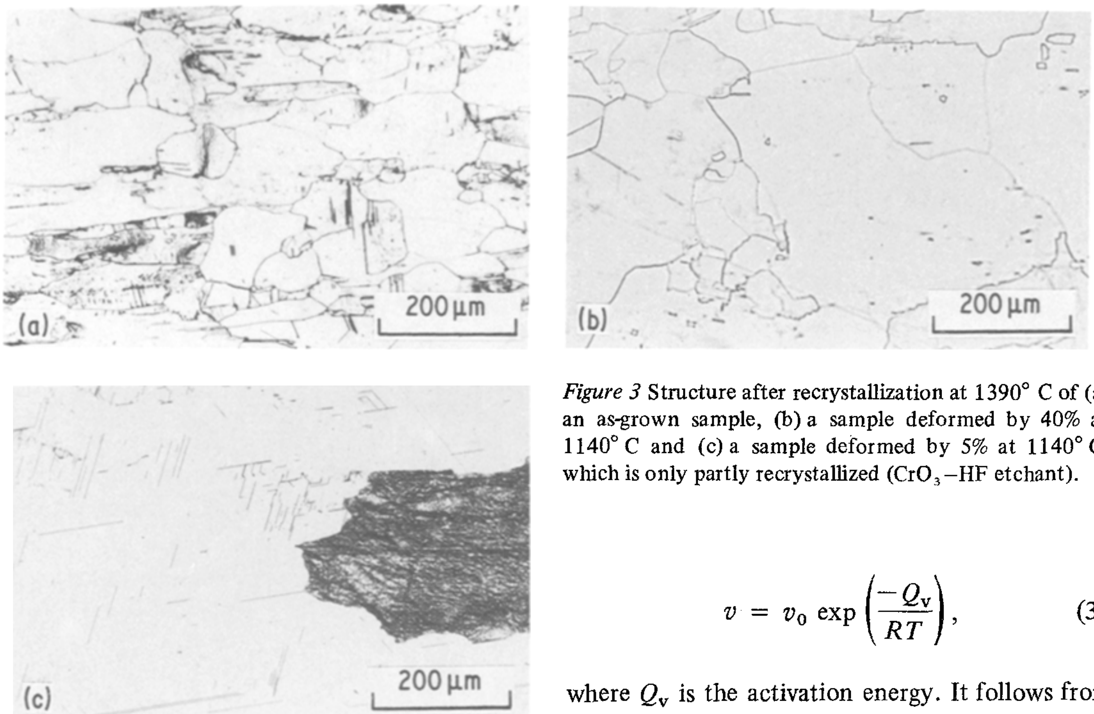

Figure 3 Structure after recrystallization at 1390° C of (a) an as-grown sample, (b) a sample deformed by 40% at 1140° C and (c) a sample deformed by 5% at 1140° C, which is only partly recrystallized (CrO_3–HF etchant).

where N is time-independent nucleation rate per unit volume, v is grain-boundary migration rate, t is time and η is the shape factor.

Because of the difficulty of measuring t_c accurately, the time needed for a 50% recrystallization (t_h) was used instead. Equation 1 then yields

$$t_h = C \cdot \frac{1}{v}, \tag{2}$$

where C is a constant. The grain-boundary migration rate, v, varies exponentially with annealing temperature according to

$$v = v_0 \exp\left(\frac{-Q_v}{RT}\right), \tag{3}$$

where Q_v is the activation energy. It follows from Equations 2 and 3 that

$$\frac{\delta \ln t_h}{\delta\, 1/T} = \frac{Q_v}{R}. \tag{4}$$

In Fig. 8 the measured values of $\ln t_h$ are plotted against $1/T$ for the two values of ϵ. Using Equation 4, the slope of the curves yield activation energies of $770 \pm 200\,\mathrm{kJmol^{-1}}$ ($\epsilon = 40\%$) and $670 \pm 200\,\mathrm{kJmol^{-1}}$ ($\epsilon = 60\%$), respectively.

The average value of the grain size after recrystallization of samples deformed between 25 and 60% is roughly a factor of 3 larger than the corresponding value of samples which were not deformed before recrystallization. Even larger

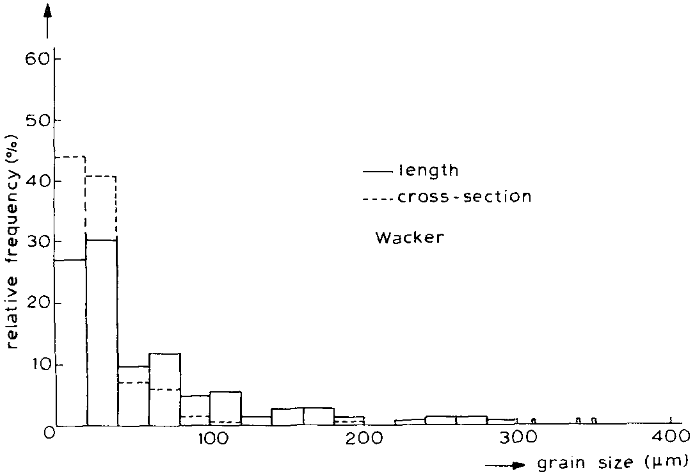

Figure 4 Distribution of larger and smaller diameter of the grains after recrystallization of as-grown material.

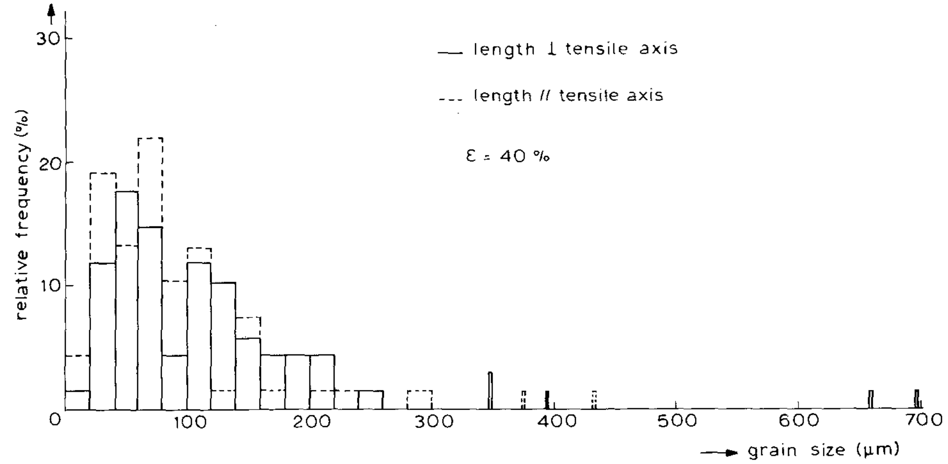

Figure 5 Distribution of larger and smaller diameter of the grains are recrystallization of a sample deformed by 40% at 1140° C.

grains could be formed after a deformation between 5 and 25% (Region II in Fig. 2). The largest grains were formed by recrystallization of samples deformed 5% (Fig. 3c). A large variation in grain size for different samples was observed. The smallest grains had average sizes ranging from 200 to 450 μm in length and 200 to 350 μm in cross-section. The largest grains observed varied between 1 and 1.7 mm in length and between 0.6 and 1 mm in cross-section with average sizes of 1.4 mm (length) and 0.8 mm (cross-section), respectively. The average length of the total number of grains in different samples varied between 0.34 and 1 mm. Instead of recrystallizing at 1390° C, a few samples were first heated at temperatures between 1000 and 1300° C for 10 to 24 h and thereafter at 1390° C until recrystallization was complete. No influence of this heat treatment on final grain size was observed. For samples annealed at 1390° C only, the time needed for a complete recrystallization of a sample deformed 5% varied from 20 to 34 h. Microscopic examination showed that the subgrain structure, in those regions which were not recrystallized yet, was not altered during the long heat-treatments applied. Values of $X(t)$ as a function of annealing temperature of a sample deformed 20% are shown in Fig. 9. From the slope of the curve ln t_h against $1/T$ (Fig. 10) an activation energy of 1450 ± 300 kJmol^{-1} was calculated (Table I). Samples deformed less than 4% (Region I in Fig. 2) did not alter their subgrain structure upon annealing. In no case was an influence of the strain rate on the resulting grain size observed. Grain growth after primary recrystallization was not found to have taken place in any of the deformed samples. The individual crystals met at angles of 120° but did not straighten their grain boundaries. All grains contained stacking faults in various numbers.

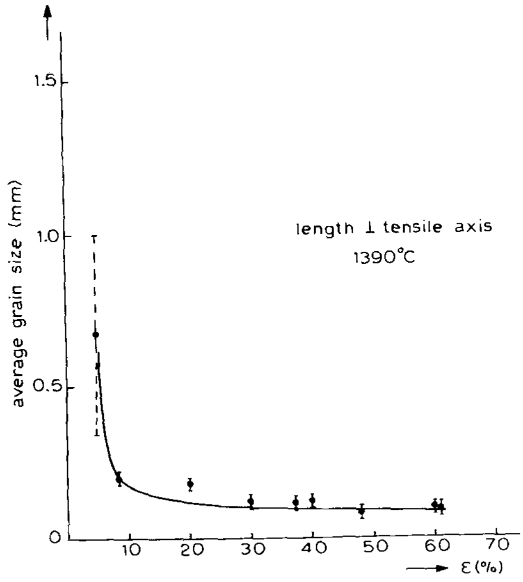

Figure 6 Average values of the larger grain diameter as a function of the degree of deformation (1140° C).

3.2. Samples deformed in compression

Samples deformed in compression developed a cell structure similar to samples deformed in tension. Because of the larger cross-section, slices of compressed samples were used for texture measurements. It was shown that deformations at 1120° C and at 1280° C up to 30%, yielded the

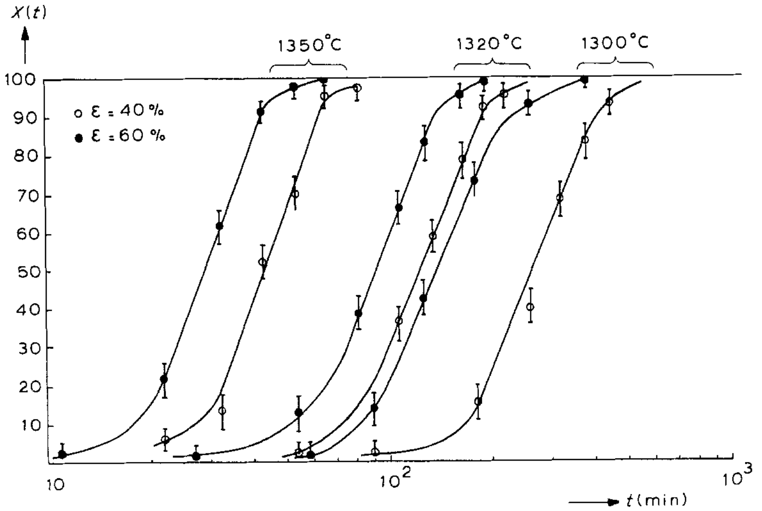

Figure 7 Recrystallized volume-fraction of samples deformed by 40 and 60% at 1140° C, respectively, as a function of annealing temperature.

same deformation texture. The ⟨1 1 1⟩ compression axis changed into a ⟨1 1 0⟩ axis and normal to it a ⟨1 1 1⟩ axis and a second, rather weak texture component developed. The latter axis was difficult to determine unambiguously due to the limited specimen area.

TEM photographs revealed gradients in dislocation concentrations inside the subgrains with a typical concentration of 2×10^{13} m^{-2} for a sample deformed 30% at 1270° C leading to a driving force for recrystallization of 1.1×10^5 Pa. The average size of the subgrains was independent of deformation temperature and degree of deformation. Upon annealing, new grains developed by nucleation and growth. The deformation texture disappeared completely. As in the case of samples deformed in tension, grain growth after primary recrystallization was very slow and consequently did not lead to grain coarsening. The dependence of grain size after recrystallization on ϵ was similar to the case of samples deformed in tension. Again the largest grains (up to more than 3 mm in cross-section) were formed in samples deformed 5%. Grain size was nearly independent of deformation temperature. Most grains contained stacking faults after recrystallization.

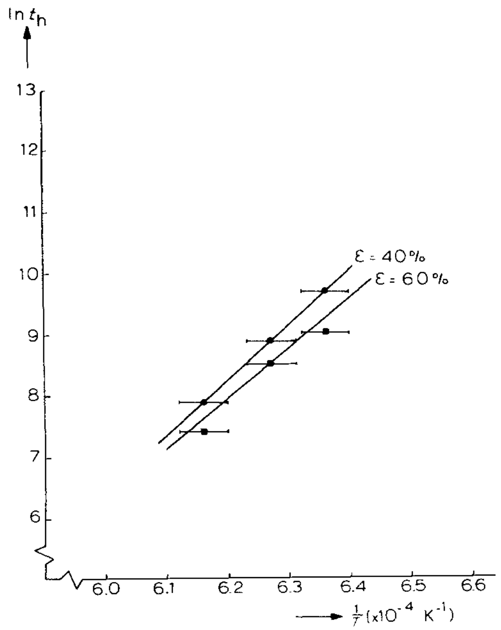

Figure 8 Logarithm of time needed for recrystallization of 50% of volume (ln t_h) as a function of reciprocal temperature ($1/T$) for samples deformed by 40 and 60% at 1140° C, respectively.

Compression of ⟨1 1 1⟩ Cz single crystals (oxygen content below the infra-red detection limit) at 1240° C with the ⟨1 1 1⟩ growth direction as the compression axis yielded a subgrain structure similar to that of CVD grown material. The misorientation of adjacent subgrains was determined by electron diffraction to be of the order of 0.1 to 0.3 degrees, corresponding with 5×10^8 m^{-1} dislocations per unit of length of sub-boundary.

Upon annealing, the subgrain structure of samples deformed between 10 and 30% was completely recrystallized into a large-grained polycrystal with grain sizes varying from 0.3 to 7 mm. Grain boundaries were relatively straight when compared with CVD grown material. After the stage of primary recrystallization some grain growth was observed. About 70% of the newly formed high-angle grain boundaries migrated during a relatively short time with an average rate of 2 μm min^{-1}, which, however, did not lead to significant grain coarsening. In some cases one could observe a small

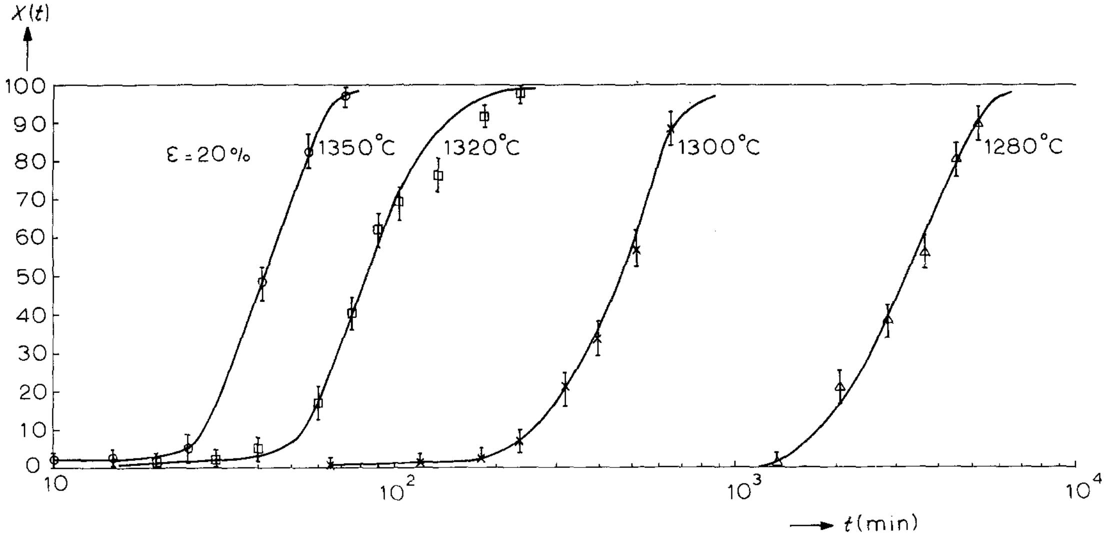

Figure 9 Recrystallized volume-fraction of a sample deformed by 20% at 1140° C as a function of annealing temperature.

grain growing at the expense of its larger neighbouring grain.

SILSO large-grained ingot crystals also developed a subgrain structure during deformation. Upon annealing, new grains nucleated at existing grain boundaries, possibly by strain-induced boundary migration (Fig. 11). The average grain size after recrystallization of a sample compressed by 29% at 1200° C had decreased by a factor of 2 compared with as-grown material. After 45 min of heating, primary recrystallization was complete. Prolonged heating led to further migration of about 5% of grain boundaries with an average rate of $1.5\,\mu\mathrm{m\,min}^{-1}$. This did not cause significant grain coarsening. The grains kept their irregular shapes and small grains remained. The concentration of lattice defects (dislocations, stacking faults) had increased during annealing.

4. Discussion

The grain size of CVD grown samples which were deformed and recrystallized is determined entirely by the number of nuclei formed. After the growing grains impinge on each other, no further grain growth is observed. As generally observed for a variety of metals [5], the largest grains are formed at low values of ϵ (about 5%) as a result of the limited number of nucleation sites. Whereas at these low strains nucleation comes about relatively rapidly, growth of nuclei is relatively slow (low driving force) which accounts for the long time needed to complete recrystallization. As a result of

TABLE I Measured activation energies as a function of ϵ

ϵ (%)	Q_V (kJ mol^{-1})
20	1450 ± 300
40	770 ± 200
60	670 ± 200

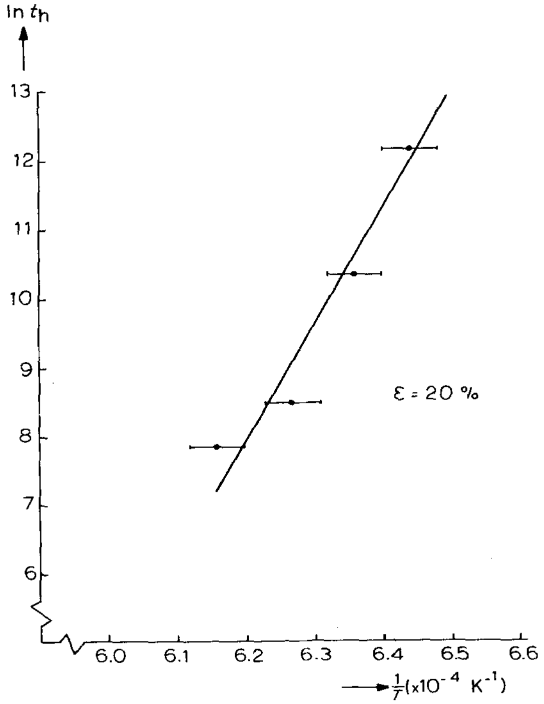

Figure 10 Logarithm of time needed for recrystallization of 50% of volume (ln t_h) as a function of reciprocal temperature ($1/T$) for a sample deformed 20% at 1140° C.

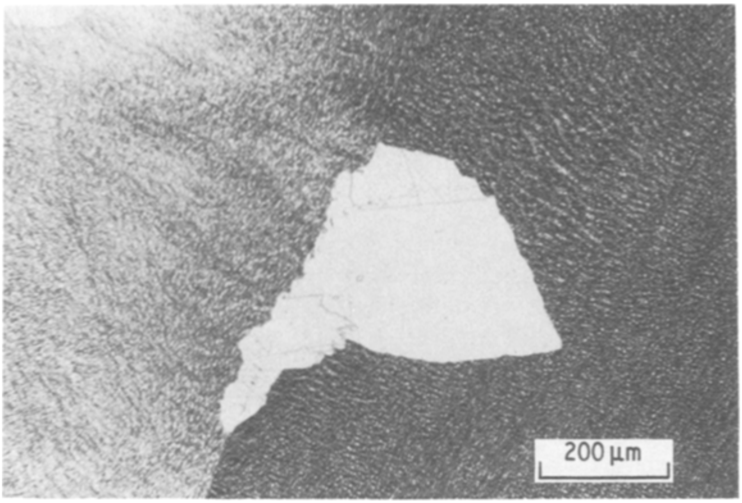

Figure 11 Nucleation of new grains (possibly by strain-induced boundary migration) during annealing at 1390° C in a SILSO sample deformed 20% at 1200° C.

this low growth rate all potential nuclei are given the possibility to develop at all annealing temperatures between 1250 and 1390° C resulting in uniform grain size. The large variation in average grain size after recrystallization of several samples deformed by 5% is probably due to inhomogeneous deformation. Since below a deformation of 4% no recrystallization occurs (critical degree of deformation), the number of potential nuclei in regions deformed between 4 and 5% is very sensitive to the exact amount of deformation. As a consequence of this possible variation in the amount of nuclei, grain size will, as observed, be inhomogeneous.

The large value of the activation energy of recrystallization at low strain values (1450 ± 300 kJmol^{-1} for a sample deformed by 20% at 1140° C) will be due probably to the high activation energy of nucleation, as also observed for a large variety of metals [5]. As the strain value is increased the activation energy decreases (670 ± 200 kJmol^{-1} for a sample deformed by 60% at 1140° C) to a value that approximates to the activation energy of the volume self-diffusion in silicon (480 kJmol^{-1}, [6]). As heating at relatively low temperatures (1000 to 1280° C) for long periods (10 to 24 h) does not influence grain size, it is unlikely that much recovery occurs prior to recrystallization. This is emphasized by the observation that the time to complete recrystallization is not changed either. All samples are recrystallized before deformation with an inherent texture change from ⟨1 1 0⟩ into ⟨1 1 1⟩. Upon compression at 1120 and 1280° C up to 30% the ⟨1 1 1⟩ fibre texture is changed into a deformation texture with a ⟨1 1 0⟩ axis parallel to the compression axis and two axes (⟨1 1 1⟩ and a second, rather weak component) normal to this ⟨1 1 0⟩ axis. Pratt *et al.* [7] compressed the same kind of material in a direction normal to the growth direction. The observed deformation texture also has a ⟨1 1 0⟩ axis parallel to the compression axis and a ⟨1 1 1⟩ component normal to this axis. The authors try to explain the components of this deformation texture by assuming that each crystal within the polycrystalline assembly deforms independently. In their observations, however, they do not take into account the change in texture upon recrystallization of the samples before they are compressed [2].

When the results on compression of Cz single crystals as obtained by Mardesich *et al.* [8] are compared with the results obtained here it can be concluded that the choice of the compression axis determines the amount of lattice deformation. Mardesich *et al.* [8] compressed (1 0 0) crystals at 1325° C but did not observe nucleation and growth upon annealing of samples deformed by less than 100%. The authors believe this to be the result of a decrease of strain energy by polygonization. However, crystals compressed along a ⟨1 1 1⟩ axis at 1240° C (this work) show nucleation and growth after 10% deformation although in this case development of subgrains during deformation is also observed.

Kinoshita and Champier [9] deformed SILSO material at 800° C in tension (12%). They did not observe significant grain growth after primary recrystallization either and grain boundaries kept their irregular shapes after annealing for 23 h at 1395° C. Grain growth in silicon seems to proceed only very slowly in all kinds of silicon (CVD, Cz and SILSO). This is probably due to the relatively low mobility of high-angle grain boundaries in covalently bonded materials. During primary recrystallization this low mobility is compensated for by a high value of the driving force. When the grains have impinged on each other the driving force is decreased by several orders of magnitude.

5. Conclusions

Dislocations formed during tension or compression of CVD-grown polycrystalline silicon at temperatures above 1100° C rearrange into a cell structure. Upon annealing at 1250 to 1410° C, all samples deformed at 1100 to 1310° C by between 5 and 60%, recrystallize by nucleation and growth. Samples deformed by between 25 and 60% recrystallize completely within a few minutes at 1390° C. The grains are irregularly shaped and inhomogeneous in size with an average value of 100 μm for samples deformed at 1140° C. For samples deformed at 1140° C by between 5 and 25% the time needed to complete recrystallization increases with decreasing strain to a value of 34 h for a sample deformed by 5%. In the latter samples, grains up to 1.7 mm in size were observed. Below a deformation of 4% no recrystallization occurs (critical degree of deformation). For the recrystallization process of samples deformed by 20 and 60% at 1140° C activation energies of $1450 \pm 300\,\mathrm{kJ\,mol^{-1}}$ and $770 \pm 200\,\mathrm{kJ\,mol^{-1}}$ were found, respectively. As in the as-grown material, grain growth after primary recrystallization of deformed material is extremely slow. Also, deformed Czochralski and SILSO ingot show limited grain growth upon annealing. This is believed to be due to a low mobility of high-angle grain boundaries in covalently debonded materials.

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