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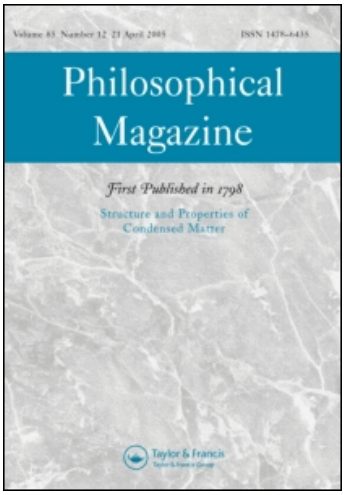

Philosophical Magazine
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713695589

Solid phase epitaxial regrowth of amorphous silicon is not affected by structural relaxation

S. Roorda[a]; Y. Lavigueur[a]
[a] Département de Physique, 2900 Boulevard Edouard Montpetit, case postale 6128 Succursale Centre-ville, H3C 3J7 Montréal, QC, Canada

First published on: 30 June 2010

To cite this Article Roorda, S. and Lavigueur, Y.(2010) 'Solid phase epitaxial regrowth of amorphous silicon is not affected by structural relaxation', Philosophical Magazine,, First published on: 30 June 2010 (iFirst)
To link to this Article: DOI: 10.1080/14786435.2010.493167
URL: http://dx.doi.org/10.1080/14786435.2010.493167

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Philosophical Magazine
2010, 1–8, iFirst

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Solid phase epitaxial regrowth of amorphous silicon is not affected by structural relaxation

S. Roorda* and Y. Lavigueur

Département de Physique, 2900 Boulevard Edouard Montpetit, case postale 6128 Succursale Centre-ville, H3C 3J7 Montréal, QC, Canada

(*Received 26 January 2010; final version received 10 May 2010*)

A piece of amorphous silicon made by self-ion implantation was structurally relaxed by thermal annealing at 650°C; subsequently, half of the sample was re-implanted to bring it back to a non-relaxed state. The sample was next submitted to a series of low-temperature anneals (425–435°C) in order to induce solid phase epitaxial crystallization and the growth rate was measured on both halves of the sample. No difference was found within an uncertainty of ±3%, which would imply that the activation energy for solid phase epitaxial regrowth remains constant to within 2 meV under structural relaxation.

Keywords: amorphous silicon; structural relaxation; solid phase epitaxial growth; activation energy

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1. Introduction

Pure amorphous silicon (a-Si), when in contact with a crystalline silicon seed, is known to crystallize epitaxially in the solid phase by a process (SPE) extremely well described by a single activation energy of $E_a = 2.70 \pm 0.02$ eV [1,2]. The simple Arrhenius equation holds over a range of nearly 1000°C, covering ten orders of magnitude in recrystallization velocity. The rate-limiting step has been argued to be related to the nucleation of a new crystal plane or step [3] but in any case represents an energy barrier between a number of atoms in the initially amorphous state and the same atoms in a slightly different configuration, recognized in transition state theory as the activated complex. Figure 1 depicts a schematic representation of this process with the solid line indicating the local and overall thermodynamic minima corresponding to amorphous and crystalline silicon as well as the activated state. When the activated complex proceeds to the crystalline side, an amount of energy is released and this not only recuperates the energy invested in creating the activated complex, but moreover results in a net heat release corresponding to the heat of crystallization [4]. Now amorphous silicon also exhibits a phenomenon known as structural relaxation (resulting in a state indicated in Figure 1 by the dashed line), and in the course of that process a considerable heat of relaxation (0.4 eV/atom) is

*Corresponding author. Email: sjoerd.roorda@umontreal.ca

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DOI: 10.1080/14786435.2010.493167
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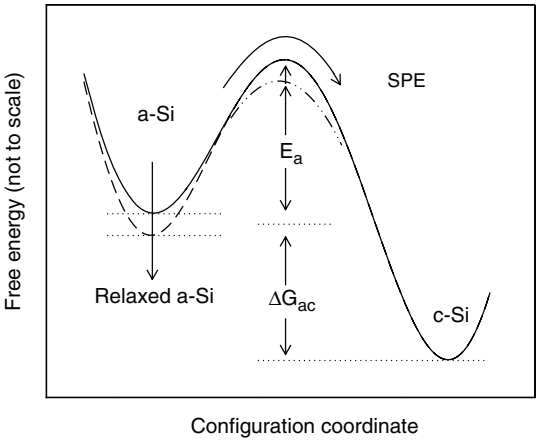

Figure 1. Schematic presentation of the thermally activated crystallization of amorphous silicon showing the Gibbs free energy (not to scale) of amorphous silicon before and after structural relaxation and crystalline silicon versus a ''configuration coordinate''.

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released [5], which amounts to about one third of the heat of crystallization (1.2 eV/atom).

As the epitaxial crystallization of amorphous silicon continues to be studied [6–8], an obvious question that arises is, does the energy barrier for solid phase epitaxial crystallization increase when the material relaxes or does it remain at 2.70 eV (as indicated by the dash-dotted line in Figure 1). Intuitively, and tracing back the atomic trajectories from the freshly crystallized state to the activated complex, one would expect the activation energy to increase as a result of structural relaxation. The experimental difficulty in answering this simple question lies in the temperature dependence of crystallization and relaxation: relaxation (characterized by a range of activation energies [5]) sets in at much lower temperatures than crystallization, and all crystallization measurements are essentially done on amorphous silicon, which is ''well relaxed'' at the crystallization temperature. It is for this reason that an earlier attempt to determine the effect of relaxation on crystallization found no difference, even if such a difference would exist [9,10]. In this paper, an experiment is described in which amorphous silicon was first relaxed at a relatively high temperature of 650°C; subsequently its crystallization velocity at 425°C was compared to that of amorphous silicon that had not been exposed to such a high temperature (or rather, which had been re-irradiated with energetic ions so as to ''un-relax'' the material). Whereas some relaxation will occur during the 425°C anneal, the ''un-relaxed'' material should not become as relaxed as the material that had been relaxed at 650°C. Our results show that the recrystallization velocity remains the same to within 3%, which would imply that the activation energy remains constant to within less than 2 meV.

2. Sample preparation

A piece of a Czochralsky grown, undoped, [001] oriented, crystalline silicon wafer was irradiated with Si ions with energies of 100, 300, 600 keV and 2 MeV to fluences

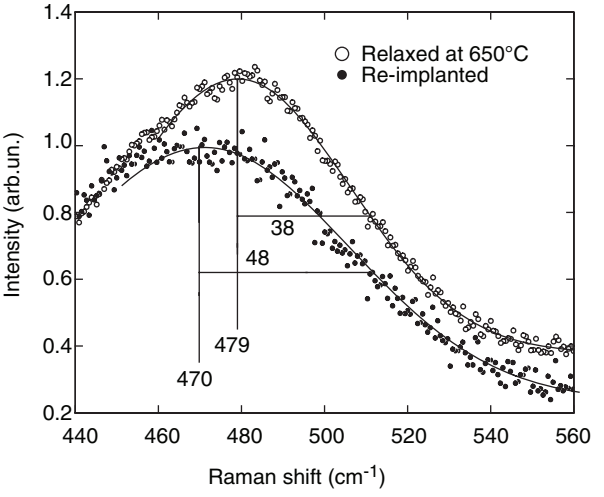

Figure 2. Raman scattering intensity for relaxed amorphous silicon (open circles) and re-implanted amorphous silicon (solid circles). Solid lines are the result of Gaussian fits to the data and were used to determine the position and half-width at half-height of the TO-like band, indicated by thin solid lines.

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of 3.5, 1.75, 0.5 and 3×10^{15} ions/cm^2, respectively. During the irradiation, the wafer was heat sunk to a sample holder held at liquid nitrogen temperature. This procedure resulted in a surface layer of around 2 μm thickness of pure amorphous silicon in intimate contact with the untouched underlying crystalline substrate. Raman spectroscopy of 532 nm light (not exceeding 300 mW) in backscattering geometry dispersed by a double spectrometer coupled to a CCD camera revealed the broad bands characteristic of amorphous silicon, showing that the surface layers had indeed turned amorphous. The piece of Si was annealed in a rapid thermal anneal system based on halogen light heating for a few seconds at a nominal temperature of 650°C, which resulted in solid phase epitaxial regrowth of more than half the thickness of the ion implanted layer and simultaneously in the thorough structural relaxation of the remaining amorphous silicon. The extent of structural relaxation can be evaluated by measuring the half width (on the right hand side) of the TO-like band in the Raman spectrum, which is shown as open circles in Figure 2. By fitting a Gaussian to this TO-like band we found its position and half-width at half-height to be 478.9 ± 0.3 and $37.6 \pm 0.3\,\mathrm{cm}^{-1}$, which are indeed high and narrow values, respectively, for amorphous silicon [11] demonstrating that structural relaxation has indeed occurred. We also notice the absence of any sharp peak near $521\,\mathrm{cm}^{-1}$, which would indicate the presence of crystalline material; this shows that SPE can proceed freely and is not in competition with random nucleation and grain growth.

One half of the sample was covered to protect it from further ion bombardment while the sample was again exposed to ion irradiation at liquid nitrogen temperature, this time to a single-ion implantion of 3×10^{15} Si ions/cm^2 at 250 keV. At this energy, most of the ion damage (often expresed as ''displacements per atom'', or dpa) is well below the surface and the bottom half of the remaining amorphous silicon is

expected to be returned to its ''as-implanted'' state by this treatment. A much smaller amount of energy is deposited close to the surface, but this is enough to induce some ''un-relaxation'' as was confirmed by, again, Raman spectroscopy. Since the absorption coefficient of a-Si at the wavelength used for Raman spectrocopy is larger than $10^5\,\mathrm{cm}^{-1}$ [12,13], only the near-surface layer of the a-Si thin film was probed; therefore, the true extent of un-relaxing will be underestimated by the Raman peak width. The solid circles in Figure 2 show the spectrum measured on the uncovered half after un-relaxation and the Gaussian fit to determine the peak position and half-width of this band. The position has shifted to a smaller Raman shift of $469.8 \pm 0.3\,\mathrm{cm}^{-1}$, whereas the TO-like band has broadened to $48.2 \pm 0.4\,\mathrm{cm}^{-1}$, which shows that indeed the amorphous silicon is not nearly as relaxed as the covered half.

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3. Recrystallization results

In order to measure the crystallization velocities, the entire piece was repeatedly annealed in a quartz tube vacuum furnace, for several hours at a time and at nominal temperatures between 425 and 435°C. After each anneal, the thickness of the remaining amorphous silicon layer was measured by Rutherford backscattering spectrometry in conjunction with channeling following the method used by Csepregi et al. [14]. He ions of 2 MeV were incident along the [001] axis of the sample and backscattered through 170°. The energy spectrum, measured before the SPE anneal treatments, of ions thus backscattered is shown in Figure 3 as circles (open circles for the relaxed a-Si and solid circles for the re-implanted a-Si). Backscattering from the free Si surface occurs near channel 561; the depth scale indicated is approximate

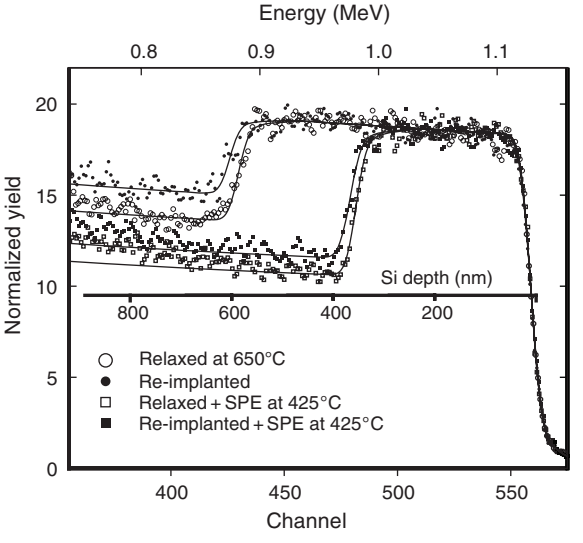

Figure 3. RBS/channeling spectra of a selection of samples. Open symbols: relaxed amorphous silicon. Solid symbols: re-implanted amorphous silicon. Circles: before recrystallization. Squares: after 224 h of crystallization.

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and based on the surface approximation. The solid lines also shown in Figure 3 are the result of fitting the spectra by optimizing the thickness of the remaining a-Si layer, the interface sharpness, and the channeled yield (modeled by diluting the Si substrate with He) using the PERT routine built into the RUMP analysis program [15,16].

The obvious change in number of backscattered ions near channel 440 corresponds to the position of the interface between the underlying crystalline substrate (where ions can channel and have a reduced backscattering probability) and the yet uncrystallized amorphous silicon (where the backscattering intensity reaches the "random" height). The interface is located at a depth of 564 ± 2 nm for the relaxed amorphous silicon and 580 ± 3 nm for the re-implanted part of the sample. The small difference in the position of the interface (26 ± 4 nm) is much more than can be attributed to the extra atoms from the un-relaxing implantation (0.6 nm), which indicates that the energy of 250 keV for the "un-relaxing" implant had been chosen too high resulting in some amorphization and end-of range damage beyond the original, sharp c-Si/a-Si interface. A further indication that the end-of-range of the 250 keV ions is beyond the original interface is the slightly changed slope of the interface: the new interface is not as sharp as the original interface.

The square symbols in Figure 3 depict two spectra after multiple anneals of several (15–21) hours at a nominal temperature of 425–435°C. Again, the open symbols correspond to relaxed, and the solid symbols to re-implanted material. The difference in interface position has reduced to 14 ± 2 nm but still exists. Since both types of material (relaxed and re-implanted) were part of one and the same sample, the thermal treatment during the recrystallizing anneals can safely be viewed as identical, yet it appears that the re-implanted material regrows slightly faster, after all the difference in interface position has narrowed by 10 nm. In order to evaluate carefully the difference in regrowth rate, if any, we have measured the RBS/channeling spectra for 12 intermediate anneal treatments and measured the interface positions after each anneal.

During the anneal treatments, the temperature was continuously monitored by a thermocouple in close proximity to the sample, and slight temperature variations of a few degrees were noted. For each anneal treatment, the amount of expected recrystallization was determined from the measured temperature–time profile and the singly activated velocity of solid phase epitaxy using 2.70 eV for the activation energy and 4.33×10^8 cm/s as prefactor. By comparing the amount of regrowth on the relaxed side of our sample (since this side of our sample should behave as stable amorphous silicon) with the expected regrowth, we noted a systematic difference which we attributed to an error in the thermocouple reading of 4°C. The temperature readings were corrected and the amount of expected regrowth was recalculated. Figure 4 shows the regrowth rate on both areas of the sample versus the expected regrowth. The sequence of points from left to right thus corresponds to subsequent anneal treatments and RBS measurements. A clear and systematic difference is evident between the amount of regrowth on well relaxed and re-implanted amorphous silicon only for the first two points close to the initial interface (left hand side of Figure 4). Therefore, the apparent enhanced regrowth rate only occurs during the first recrystallization anneal treatments when the recrystallizing material is not re-implanted amorphous silicon, but freshly damaged c-Si near the

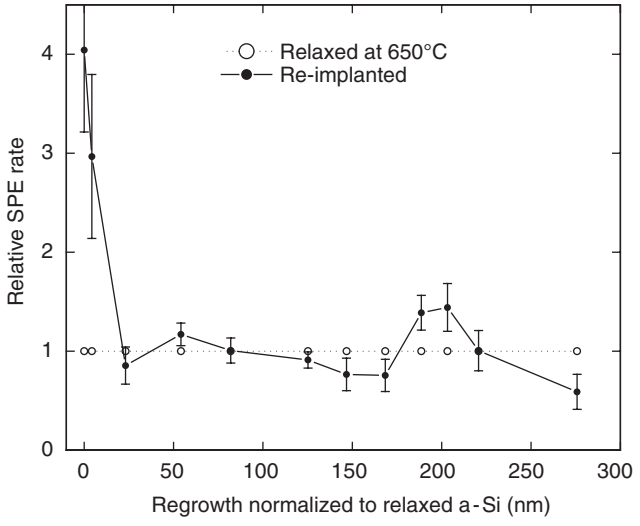

Figure 4. SPE regrowth rate of re-implanted amorphous silicon (solid symbols) at a nominal temperature of 425°C normalized to the regrowth rate in well-relaxed amorphous silicon (open symbols).

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end-of-range of the 250 keV Si ions. With RBS/channeling the end-of-range damage cannot be distinguished from amorphous silicon, but several other experimental techniques, e.g. X-ray [17] and optical [18] have shown that beyond the a-Si/c-Si interface highly defected c-Si is present. Some of this damage is known to anneal at temperatures well below that required for epitaxy of amorphous silicon [19], and therefore we attribute the first two data points in Figure 4 to the removal of end-of-range damage and *not* to an enhanced SPE rate.

For all other points in Figure 4, beyond 20 nm regrowth, the regrowth rates on both halves of the sample are identical to within ±1–3% as is determined by calculating the average regrowth rate and its standard deviation over all but the first two points. After the last data point, the remaining material was again characterized by Raman spectroscopy and the results are shown in Figure 5. The symbols and lines in Figure 5 are as in Figure 2, except that squares are used instead of circles. The half-widths and positions of the TO-like band were $48.9 \pm 0.2\,\mathrm{cm}^{-1}$ (re-implanted) and $40.6 \pm 0.2\,\mathrm{cm}^{-1}$ (relaxed) and $474 \pm 0.2\,\mathrm{cm}^{-1}$ (re-implanted) and $478.9 \pm 0.2\,\mathrm{cm}^{-1}$ (relaxed); the entire sequence of recrystallization anneals did not result in a significant change in Raman parameters of either side of the sample. As well, the Raman spectra do not show any indication of the presence of crystalline silicon; even a small number of crystalline grains would lead to a detectable sharp peak near $521\,\mathrm{cm}^{-1}$ [20]. We therefore conclude that all points shown in Figure 4 indeed refer to two types of amorphous silicon in a different state of relaxation and thus the solid phase epitaxial regrowth rate of amorphous silicon at 425°C is identical to that of amorphous silicon which had been relaxed at 650°C.

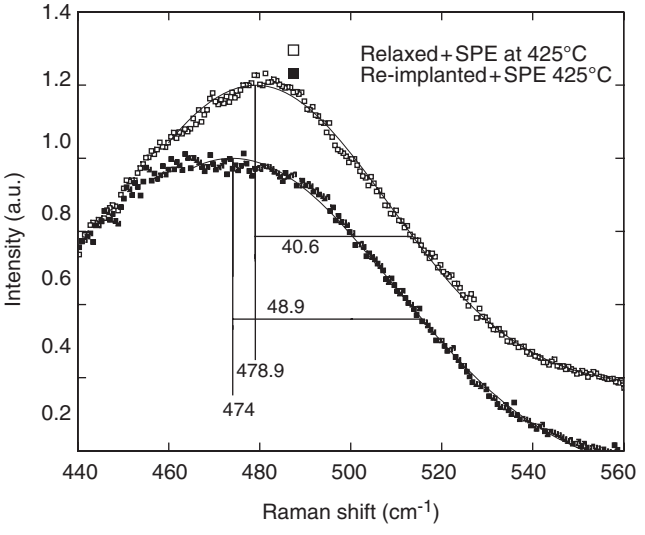

Figure 5. Raman scattering intensity for relaxed amorphous silicon (open squares) and re-implanted amorphous silicon (solid squares) after all recrystallization anneal treatments. Solid lines are the result of Gaussian fits to the data and were used to determine the position and half-width at half-height of the TO-like band, indicated by thin solid lines.

If an enhancement or reduction of the SPE rate by a factor 1.03 were solely due to a change in the activation energy, then the required change would be less than 2 meV. We can thus conclude that the activation energy for SPE of amorphous silicon would not be affected by structural relaxation to within 2 meV. Or, in words going with Figure 1, the dash-dotted line follows the dashed line to within 2 meV.

Two different views of structural relaxation of amorphous silicon exist. One view is that all atoms contribute equally, and structural relaxation is (nearly fully) characterized by a reduction in average bond angle distortion [21,22]. Alternatively, it has been argued that the distinction between relaxed and non-relaxed amorphous silicon is similar to the difference between (near-)perfect crystalline silicon and c-Si containing a high density (around an atomic %) of point defects and point defect complexes [5]. The latter model would be expected to have less effect on the energy barrier for solid phase epitaxial crystallization and thus appears more compatible with the present experimental results.

4. Conclusion

The solid phase epitaxial regrowth rate induced by low temperature (425–435°C) thermal annealing of amorphous silicon is the same within ±1–3% for amorphous silicon that had been structurally relaxed at 650°C and amorphous silicon "as implanted". This implies that the activation energy for solid phase epitaxial crystallization of amorphous silicon would remain constant to within 2 meV under structural relaxation.

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Acknowledgements

It is a pleasure to thank L. Godbout and X. Perraton for their expert support of the accelerators, and R. Leonelli and G. Bentoumi for assistance with the Raman measurements. This work was financially supported by FQRNT (Fonds québecois de la recherche sur la nature et la technologie) through the grant to the RQMP (Regroupement québecois sur les matériaux de pointe) and by NSERC (Natural Sciences and Engineering Research Council of Canada).

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