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ASPECTS OF SILICON CRYSTALLIZATION

W.C. SINKE and S. ROORDA

FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

Recent experiments concerning structural relaxation of amorphous Si and epitaxial regrowth of micro-crystalline Si are reviewed. The first experimental evidence for a heat release from amorphous Si prior to crystallization, as obtained using calorimetry, is presented and these results are compared to predictions made on the basis of results from Raman spectroscopy and other techniques. It is shown that micro-crystalline Si formed by explosive crystallization of amorphous Si can be regrown epitaxially on a single-crystal substrate via a two-step process. Initially, regrowth occurs fast and at temperatures well below those required for regrowth of poly-crystalline silicon deposited by chemical vapour deposition. Subsequently, the regrowth rate slows down and saturates at a level typical for epitaxial alignment of poly-crystalline Si.

1. Introduction

Silicon is a key material in today's semiconductor industry. For that reason many properties of silicon have been studied intensively over the past decades. As far as crystallization is concerned, particular attention has been paid to solid-phase epitaxy (SPE) of amorphous silicon (a-Si) on a single-crystal silicon (c-Si) substrate. SPE is used for the regrowth of a-Si formed during ion implantation into c-Si [1]. The general features of SPE have been described over a very wide range of temperatures (≈ 500 to $\approx 1350\,^\circ$C) and are now reasonably well understood [2]. Besides SPE, there are several other processes related to silicon crystallization which are of fundamental interest and which have not been studied in much detail.

During the heating phase prior to crystallization, the structure of a-Si changes from the as-implanted or as-deposited state to another state with different properties [3]. This phenomenon is called structural relaxation, however, its exact nature has not yet been established. Relaxation is the precursor of crystallization and therefore understanding of the atomic rearrangements associated with relaxation may help to understand crystallization in more detail.

SPE of a-Si on c-Si may be regarded as a model process for the study of single-crystallization of Si, but also poly-crystalline Si (p-Si) or micro-crystalline Si (μc-Si) layers can be recrystallized on a c-Si substrate [4,5]. This latter process is strongly dependent on the type of p-Si or μc-Si used and shows both similarities and differences with SPE of a-Si.

In this paper we will briefly review recent experiments concerning structural relaxation of a-Si and solid-phase regrowth of p-Si and μc-Si.

2. Structural relaxation of amorphous silicon

a-Si has been studied for roughly two decades now. Research was triggered both by fundamental interest concerning the network-structure of a-Si and by the fact that a-Si became technologically important with the introduction of ion implantation as a method to introduce dopant atoms in c-Si [6]. In contrast to c-Si, a-Si is not a well-defined material. It is mainly described by what it is not. Clearly a key property of a-Si is the absence of long-range structural order. A model which has been successful in explaining some of the main features of a-Si is the "continuous random network" model (CRN) [7]. In a CRN, the local atomic order resembles that in c-Si, but the overall structure is totally different from that of c-Si. This is mainly due to relatively small ($\approx 10\%$) deviations from the ideal tetrahedral bond angle

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(109.5°) and to a large freedom of rotation around bonds between adjacent atoms. As a result of the local deformations a-Si contains a strain energy of roughly 10 kJ/mol. This energy is usually ascribed to bond-angle distortions and to a smaller extent, to bond-length distortions, bond rotations and (point) defects [8].

Ever since a-Si has been studied, it has been recognized that many of its properties vary strongly with preparation conditions and subsequent thermal treatments [9]. Among these are optical, electrical and electron spin properties. An interesting question in relation to these variations is whether or not they are correlated to changes in the strain energy stored in the a-Si network. This is important, since strain energy constitutes the major part of the difference in free energy between a-Si and c-Si, which in turn determines the driving force for crystallization. Calorimetry studies of crystallization of ion-implanted a-Ge and a-Si have indicated that a-Ge does show a clear lowering of strain energy upon heating, while a-Si does not [10]. This is somewhat surprising in view of the structural similarity of a-Ge and a-Si and the fact that the two materials behave qualitatively the same in many ways [8]. It is noted, however, that the experiments in ref. [10] were undertaken mainly with the aim to study crystallization and no specific attempt was made to prove or disprove a release of heat from a-Si prior to crystallization. In contrast to these calorimetry experiments, Raman spectroscopy of a-Si has consistently indicated that the average bond-angle distortion and hence, the strain energy stored in the random network, does decrease upon annealing [11–16]. This is true for both vacuum-deposited and ion-implanted a-Si. Raman spectroscopy, however, has the disadvantage of being a rather indirect probe of structural properties. Considerable interpretation is needed to translate information on dynamical network properties as contained in the Raman spectrum into information concerning the static network structure, such as bond-angle distortion [8]. Although most authors agree on the qualitative relation between the a-Si Raman spectrum and the network structure, there is no agreement on the absolute numbers involved. Estimates based on Raman results of the maximum difference in strain energy between as-prepared a-Si and fully relaxed a-Si roughly range from 4 kJ/mol [15] to 20–30 kJ/mol [11]. These numbers should be compared to a heat of crystallization of a-Si of ≈ 12 kJ/mol (for fully relaxed material). More direct information on changes in bond-angle distortion upon annealing has recently been obtained by neutron diffraction [17]. These experiments indicate that the expected heat of relaxation is in the lower end of the range given above, although it is difficult to extract absolute numbers due to the uncertainty in the elastic constants which couple bond-angle distortion to strain energy.

Conclusive evidence for a release of heat upon structural relaxation as well as absolute numbers can only be obtained by calorimetry. a-Si is usually prepared in thin-film (< 1 μm) form and is therefore only available is small amounts in terms of the material needed for accurate calorimetric measurements. Thick films may be prepared, for instance by sputtering, but are not of high quality since they contain voids and impurities. These constraints have hampered calorimetry experiments on a-Si until now.

An alternative for the preparation of a-Si is high-energy ion implantation into c-Si. With this technique it is possible to prepare clean, void-free and thick (up to ≈ 5 μm) layers of a-Si. Using samples thus prepared, a relatively large amount of a-Si can be stacked in the calorimeter head and it becomes possible to measure the very small amounts of heat which are released upon relaxation of a-Si. Recently we have employed this method to prepare a-Si samples optimized for calorimetric measurements [18]. c-Si wafers of 200 μm thickness and polished on both sides have been implanted on front and back with 0.5, 1.0 and 2.0 MeV ^{28}Si or ^{40}Ar ions. The total dose was 5×10^{15} and 2×10^{15} cm^{-2}, respectively. During implantation the sample holder was cooled using liquid nitrogen and the ion beam was scanned electrostatically over the sample surface. This yielded a-Si layers of ≈ 2.2 μm thickness, as determined using 1 MeV H^+ Rutherford backscattering spectrometry (RBS) and channeling. A second type of sample was prepared by implanting c-Si sheets of 20 μm total thickness on one side using the same recipe as described above.

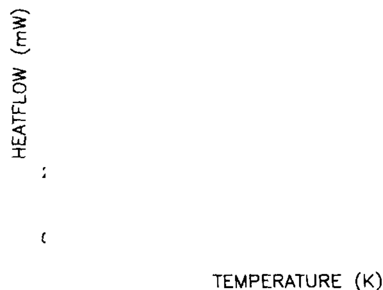

Fig. 1. DSC traces for (a) c-Si, (b) a-Si which has been pre-annealed to 813 K and (c) as-implanted a-Si. Curves (b) and (c) have been shifted for clarity over 2 and 4 mW, respectively (after ref. [18]).

Fig. 1 shows typical traces as obtained using a Perkin Elmer 7 series differential scanning calorimeter (DSC) at a scan rate of 40 K/min (from ref. [18]). All measurements were performed with c-Si samples in the reference furnace and the experimental a-Si on c-Si samples in the other furnace. Curve (a) was taken with c-Si samples in both furnaces and gives an indication of power baseline stability. It is noted that the major difficulty in small-signal DSC measurements such as these is to obtain a reliable baseline. Curve (c) was measured on an as-implanted sample and curve (b) on a sample which was pre-heated to 813 K at a rate of 80 K/min, immediately followed by quenching. Both curves (b) and (c) show a peak around 950 K, which is recognized as crystallization of a-Si. The exponential increase shown by these peaks reflects thermally activated solid-phase epitaxy at the c-Si/a-Si interface, while the abrupt decrease indicates that the c-Si/a-Si interface has reached the surface and crystallization is completed. In addition to the peak at high temperatures, curve (c) shows a heat release in the range of 400–900 K. This cannot be due to crystallization and is attributed to structural relaxation of a-Si. This signal is not observed in curve (b) for the pre-heated sample, since most of the relaxation has already occurred during preheating. Clearly, the uncertainty in the area under curve (c) and hence, the amount of heat released upon relaxation is still considerable. Therefore DSC traces were taken in a narrower temperature range (not including crystallization) and at a higher scanrate of 80 K/min. In this way the baseline accuracy is improved and the heat-flow signal is increased. A series of measurements thus performed yields an average heat of relaxation of ≈ 4 kJ/mol (determined over the temperature range of 400–800 K). Scans over a wider temperature range (up to 1000 K) give a heat of crystallization of 12 kJ/mol, which is in agreement with the value of 11.9 ± 0.7 kJ/mol reported by Donovan et al. [10]. It is recognized that more accurate DSC measurements of structural relaxation in a-Si are required, but it is now for the first time demonstrated that indeed a-Si shows a one-time low-temperature heat release upon annealing. This is fully consistent with indications obtained by Raman spectroscopy [11–16], neutron diffraction [17] and IR optical spectroscopy [19,20] and shows that also in terms of heat release a-Si and a-Ge behave qualitatively the same [10,21].

3. Solid-phase regrowth of microcrystalline silicon

a-Si layers prepared by ion-implantation into c-Si or vacuum deposition onto c-Si can be single-crystallized in a layer-by-layer fashion by SPE at temperatures in the range of 500–1350 °C [2]. SPE is a thermally activated process and characterized by an activation energy of ≈ 2.7 eV, which has been related to bond-breaking and -rearrangement at the a-Si/c-Si interface, although not in detailed terms. The growth rate varies from $\approx 10^{-10}$ cm/s at 500 °C to ≈ 1 cm/s at 1350 °C. The driving force for SPE is determined by the difference in free energy between the crystalline and the amorphous phase, which in turn is mainly determined by the bond-angle distortions in the a-Si random network [8].

Besides a-Si, also p-Si layers can be regrown epitaxially on a c-Si substrate [22–25]. In contrast to SPE, regrowth of p-Si has not been studied in great detail and is not as well characterized. This is partly due to the fact that the properties of p-Si layers vary strongly with the preparation method and conditions. In addition, it is difficult to de-

posit p-Si layers on a c-Si substrate while maintaining an atomically clean interface. Impurities at the p-Si/c-Si interface disturb regrowth and are therefore undesirable if one wants to study this process in detail. The general picture which follows from the available experimental data is the following. Regrowth of deposited p-Si (typical grain size 100 nm) does only occur at temperatures > 1000 ° C. The process does not proceed in a pure layer-by-layer fashion, but rather by the formation of epitaxial columns, which grow laterally to consume the surrounding misaligned grains. This is called epitaxial alignment. The driving force for alignment is determined by the grain boundary and interface energy while the activation energy is 4–6 eV, which has been associated with Si (self) diffusional jumps across grain boundaries.

An alternative to deposition techniques for the preparation of p-Si layers on a c-Si substrate is pulsed-laser induced explosive crystallization (EC) of ion-implanted a-Si [26–31]. Using this method it is possible to prepare μc-Si layers (average grain size 5–10 nm) which are separated from the c-Si substrate by a thin layer of a-Si (see fig. 2). Both the c-Si/a-Si interface and the a-Si/μc-Si interface are free of impurities. The a-Si layer can easily be regrown by SPE at relatively low temperatures and the resulting c-Si/μc-Si structure is very suitable for the study of epitaxial regrowth of μc-Si.

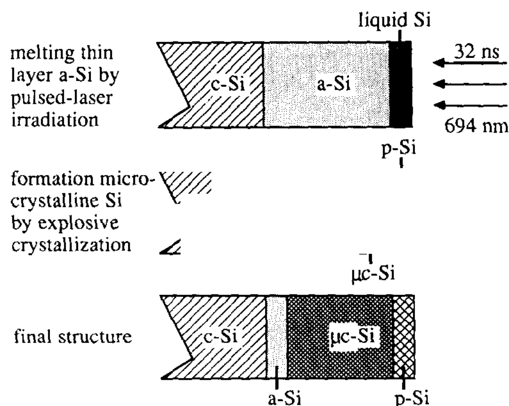

Fig. 2. Schematic picture of the formation of μc-Si layers by pulsed-laser induced explosive crystallization of a-Si.

ALIGNED LAYER THICKNESS (nm)

Fig. 3. Thickness of the epitaxially regrown μc-Si layer as a function of annealing time at different temperatures. The hatched region indicates a-Si which was not converted to μc-Si, see also fig. 2 (after ref. [4]).

a-Si layers have been prepared by 170 keV P^+ implantation into Si(100) to a dose of 4×10^{15} cm^{-2}. During implantation, the substrate holder was cooled with liquid nitrogen. This procedure yielded an a-Si layer of 320 nm thickness. Subsequently, the samples were irradiated with ruby laser pulses ($\lambda = 694$ nm, pulse length = 32 ns) at an energy density of 0.16 J cm^{-1}. This energy density is sufficient to melt a thin surface layer of a-Si and to trigger EC. The resulting structure is: c-Si substrate/55 nm a-Si/210 nm μc-Si/55 nm p-Si. The p-Si at the surface consists of grains which are considerably larger than those in the μc-Si layer underneath and is typical for layers formed by EC. Samples thus prepared were annealed at temperatures between 760 and 1000 ° C, either in a vacuum furnace (5–180 min) or a rapid thermal annealer (1–300 s) under flowing Ar. Epitaxial regrowth was monitored using 1.8 MeV He^+ RBS and channeling.

Fig. 3 (from ref. [4]) shows the thickness of the epitaxially regrown layer as a function of annealing time, for different annealing temperatures. The first ≈ 55 nm of regrowth (hatched region) corresponds to the a-Si layer between c-Si and μc-Si. The figure shows that the interface between a-Si and μc-Si is reached within ≈ 1 s for all temperatures. This is in agreement with reported values for the SPE rate [2]. Subsequently, the growth front enters the μc-Si layer. Initially (10–60 s) this occurs very fast and RBS shows that the interface

between c-Si and μc-Si remains relatively flat in this regime. Subsequently, saturation occurs and for temperatures up to 850°C the growth front does not proceed any further into the μc-Si layer. Only at 900°C or higher, growth continues at a rate which is much smaller than that in the initial stage. RBS shows that this slow growth is accompanied by roughening of the c-Si/μc-Si interface.

In an Arrhenius plot, fig. 4 shows a comparison of our growth rate results (circles) with values reported in literature for alignment of deposited p-Si and SPE of a-Si (dashed lines). Solid circles correspond to fast growth in the initial stage, as obtained from fig. 3. The solid line is a fit through the data points and corresponds to an activation energy of 2.6 ± 0.3 eV. Open circles correspond to slow growth in the saturation regime. The literature values are for layers with doping levels comparable to those in the present experiments. Fig. 4 shows that the initial growth rates of μc-Si formed by laser-induced EC of a-Si are orders of magnitude higher than those of deposited p-Si. The rates obtained after saturation, on the other hand, agree reasonably well with values for alignment of p-Si. A comparison between regrowth of μc-Si in the initial stage and SPE of a-Si shows that the latter process is always much faster, but that the activation energies for both processes are the same within the experimental error.

These observations lead to following picture of regrowth of μc-Si. The as-prepared μc-Si consists of very small grains and therefore contains a relatively large grain boundary energy. In addition, the grains are distorted and defected because of their small size and because they have been formed by rapid solidification from the melt [31]. For these reasons the difference in free energy between μc-Si and c-Si is larger than that between p-Si and c-Si and the driving force for single-crystallization is also expected to be larger. Obviously, the difference in free energy between μc-Si and c-Si is in turn smaller than that between a-Si and c-Si and the driving force for regrowth of μc-Si should be smaller than that for SPE of a-Si. From these arguments it can be roughly understood that μc-Si behaves intermediately between p-Si and a-Si in terms of regrowth. The activation energy found for fast regrowth of μc-Si suggests that the limiting process resembles that in SPE of a-Si, that is, breaking and rearrangement of Si–Si bonds rather than Si self-diffusion across grain boundaries (as has been suggested for alignment of p-Si). The observation that the interface between c-Si and μc-Si remains relatively flat during the initial stage of regrowth, suggests that grains are consumed by the substrate in a layer-by-layer fashion, which is also similar to SPE of a-Si. It has been shown that low-temperature (≈ 600°C) annealing of μc-Si results in an increase of the effective grain size and a reduction of the distortion in the grains, which leads to a lowering of the free energy difference between μc-Si and c-Si [31]. This process is also expected to occur during regrowth and therefore the driving force will decrease and the growth rate will fall, which is as observed in fig. 3. After annealing as it occurs during the initial 10-60 s fast regrowth, μc-Si behaves similar to p-Si: regrowth requires high temperatures and does no longer proceed in a layer-by-layer fashion, but is accompanied by roughening of the interface.

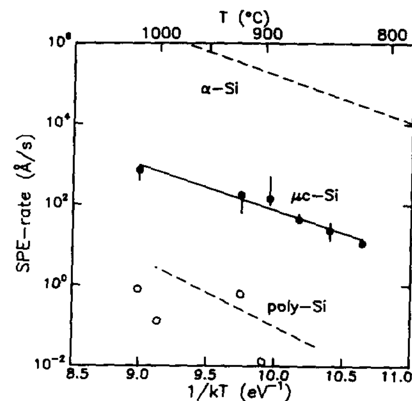

Fig. 4. Arrhenius plot (after ref. [4]) of epitaxial regrowth rates for a-Si (upper dashed line, from ref. [2]), and deposited poly-crystalline Si (lower dashed line, from ref. [24]), in comparison to data obtained on μc-Si formed by explosive crystallization of a-Si (circles). Solid circles refer to fast regrowth in the initial stage, open circles to slow regrowth after saturation (see text). The solid line represents a least-squares fit through the data points.

4. Conclusions

We have presented the first experimental confirmation of predictions that a-Si shows a heat

release during structural relaxation. Relaxation is thought to occur via a reduction of the average bond-angle distortion in the a-Si network and should therefore lead to a lowering of the elastic strain energy. The heat of relaxation amounts to ≈ 4 kJ/mol in the temperature range of 400–800 K for a-Si formed by Si or Ar ion implantation into c-Si.

Further we have shown that μc-Si layers formed by laser-induced explosive crystallization of a-Si can be regrown epitaxially on Si(100) via a two-step process. Initially, growth is very fast and occurs at temperatures well below those required for epitaxial alignment of p-Si formed by chemical vapour deposition. Regrowth rates of μc-Si in this regime are intermediate between those for SPE of a-Si and alignment of p-Si, while the activation energy is similar to that for SPE of a-Si. Subsequently, the regrowth rate slows down and saturates at a level which is typical for alignment of p-Si. This is attributed to grain growth, defect annealing and a reduction of elastic distortion in μc-Si during the initial phase of regrowth.

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