Solid-Phase Epitaxial Crystallization of Strain-Relaxed $Si_{1-x}Ge_x$ Alloy Layers

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Solid-phase epitaxial crystallization (SPEC) of Si, Ge, and strain-relaxed $Si_{1-x}Ge_x$ alloys, with x in the range 0.11 to 0.53, is investigated in the temperature range 300 to 650 °C. The activation energy for SPEC is shown not to vary monotonically with increasing Ge concentration but to increase above that of Si for Ge concentrations less than $x \leq 0.4$. This unexpected behavior is discussed in terms of existing models for SPEC.

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Solid-phase epitaxial crystallization (SPEC) of amorphous semiconductor layers has been studied extensively [1–5]. The crystallization rate of Si has been measured over a particularly wide temperature range and can be well described by an Arrhenius expression with an activation energy of 2.68 eV [2] (2.0 eV for Ge [5]). The crystallization rate of Si also depends on crystallographic orientation, being fastest in the ⟨100⟩ orientation and slowest in the ⟨111⟩ orientation, and is influenced by impurities [1], being enhanced by low concentrations (below the solid solubility limit) of electrically active impurities and retarded by inactive impurities such as O and C. At high concentrations (above or at the solid solubility limit) most impurities retard SPEC, with some being segregated at the crystalline/amorphous interface during crystallization [1]. H is an impurity of particular interest in this regard since it has been shown to migrate into amorphous Si layers from the annealing ambient during crystallization. Once in the layer, it segregates at the crystalline/amorphous interface and retards crystallization [3]. The available data suggest that SPEC is thermally activated by a bond-breaking event at the crystalline/amorphous interface [5] and that this event occurs at a specific "defect" site which can exist in a charged state. Dopants are believed to increase the SPEC rate by increasing the total concentration of these defect sites [5].

Recent experiments suggest that hydrostatic pressure and biaxial stress can also affect the rate of SPEC [4,5]. Such measurements are of particular interest since they provide information about the shape and size of defect controlling SPEC [4,5]. SiGe strained layers are useful model systems in this regard because the effect of a biaxial stress can be studied directly. SPEC of intrinsic SiGe alloy layers has been studied both for uniform alloy layers [6–11] and layers synthesized by ion implantation [12–18]. Reductions in crystallization rate and increases in activation energy have been observed in such systems and have been interpreted in terms of the effect of stress on the activation event [9,10]. However, it has also been shown [6–11,13,16–18] that while SiGe strained layers grown by molecular beam epitaxy (MBE) or chemical vapor deposition (CVD) can exceed the theoretical critical thickness by more than an order of magnitude, layers grown by SPEC generally relax at, or near, the predicted critical thickness, despite the fact that the growth temperatures (~500–600 °C) are similar in both cases. Moreover, strain relaxation during SPEC is preceded [8] by or accompanied by roughening or {111} faceting of the crystalline/amorphous interface. This complicates the interpretation of measured velocity changes and raises the question as to whether or not the reported velocity reductions and activation energy increases can be attributed to fundamental thermodynamical effects or whether they are a consequence of changes in the mode of crystallization during strain relief.

In this study, the crystallization kinetics of fully relaxed $Si_{1-x}Ge_x$ alloy layers are examined. It is shown that the activation energy for solid-phase epitaxial crystallization does not vary monotonically between that of Si and Ge with increasing Ge concentration but increases above that of Si for Ge concentrations less than about 40%.

Experiments were conducted on pure Si and Ge, and on strain-relaxed $Si_{1-x}Ge_x$ alloys of composition $x =$ 0.11, 0.12, 0.20, 0.21, 0.31, and 0.53. The alloy layers were grown epitaxially on ⟨100⟩ oriented Si substrates by either MBE or CVD. Strain relaxation was achieved by growing the 1.0–1.5 μm thick alloy layers on a compositionally graded (linearly graded from $x = 0$ to the desired composition) buffer layer. This results in near-complete strain relaxation and low threading dislocation densities in the surface layer [19]. In order to assess whether or not residual strain influences crystallization kinetics, the $Si_{0.79}Ge_{0.21}$ sample was studied with and without a high temperature preanneal. One sample was prepared from as-grown material and a second sample was annealed at 1100 °C for 1 min (using a rapid-thermal-annealing system with an Ar ambient) prior to ion implantation. This high-temperature annealing scheme was shown by double crystal x-ray diffraction (DCXRD) to relax the strain in thin (120 nm) $Si_{1-x}Ge_x$ alloy layers with $x \geq 0.085$.

Amorphous layers of approximately 400 nm thickness were created in the near-surface region of samples by ion implantation with 200 keV ^{28}Si ions to a fluence of

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1×10^{15} cm^{-2}. Samples were held at $\sim -196\,^\circ$C during implantation and were tilted $\sim 7^\circ$ from the incident beam direction to avoid ion channeling effects. (The use of a tandem accelerator and a Cs sputter ion source ensured that beam contamination from CO and N_2 was negligible.) The base pressure during implantation was better than 5×10^{-7} Torr.

Solid-phase epitaxial crystallization was monitored *in situ* using time resolved reflectivity (TRR) [2] at a wavelength of 1.523 μm. The samples were heated in air by attaching them to a preheated metal block using a small vacuum chunk. This arrangement ensures that the sample attains the desired temperature in times of ≤ 0.1 s, enabling crystallization velocities of the order of 100 nm/s to be measured. Crystallization velocities were determined over the approximate depth range 90–280 nm by measuring the crystallization time between interference extrema. The absolute sample temperature was calibrated with reference to the crystallization velocity of Si, as given by Olson and Roth [2] [i.e., $v = 3.1 \times 10^8 \exp(-2.68/kT)$ cm/s]. It should be noted that velocity measurements for Si, and SiGe alloy layers with $x \leq 0.31$, were performed over the same temperature range, 480–650 °C. This ensures that the observed changes in activation energy, relative to Si, are not sensitive to precise temperature calibration.

The amorphous layer thickness, alloy composition, and crystal quality were determined with Rutherford backscattering spectrometry and ion channeling (RBS-C) using 2.0 MeV He ions. The crystalline quality of the initial layers was also examined by transmission electron microscopy (TEM) using a JEOL 2000EX microscope operating at 200 kV. RBS-C and TEM data are not included in this paper.

Typical TRR spectra are shown in Fig. 1 for Si and a $Si_{0.79}Ge_{0.21}$ alloy layer during annealing at 633 °C. The interference maxima and minima are clearly defined and exhibit a near-constant amplitude as the amorphous layer thins due to the low absorption of the 1.523 μm wavelength light in amorphous Si. This is consistent with high-quality SPEC at an abrupt crystalline/amorphous interface, an interpretation which was confirmed by RBS-C analysis of the recrystallized material. Crystallization velocities were determined from the measured time separation of interference extrema and the corresponding depth interval in the sample, l, determined from relation $l = \lambda/4n$ for the interval between a maximum and minimum, where λ is the wavelength of the light and n is the refractive index of the layer (corrected for composition and temperature). The refractive index was determined as a function of Ge composition by comparing TRR spectra with amorphous layer thicknesses measured by RBS-C. (It should be noted that the absolute value of the refractive index affects the magnitude of the crystallization velocity but does not affect the activation energy.) The temperature dependence of refractive indices were assumed to be the same for amorphous and crystalline layers of the same composition [20]. This correction is small (changing the activation energy by < 0.01 eV) but is included in the present analysis for completeness.

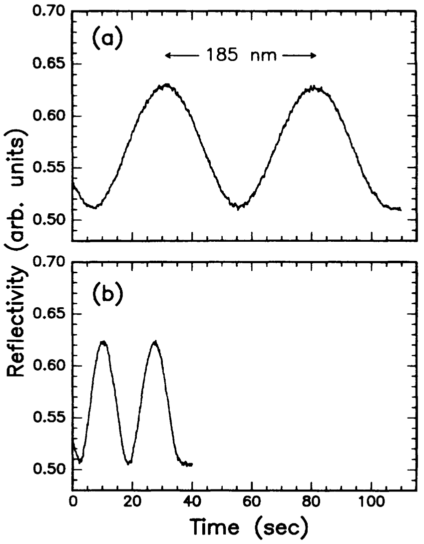

FIG. 1. TRR spectra from Si and $Si_{0.79}Ge_{0.21}$ layers during annealing at 633 °C. The depth interval l indicated on the Si spectrum was calculated from the expression $l = \lambda/2n$, where $\lambda = 1.523$ μm.

It should be noted that the crystallization velocity of thick amorphous Si layers was found to vary with depth, decreasing as crystallization proceeded to the surface. This effect has previously been shown to result from H segregation at the crystalline/amorphous interface [3]. To assess the role of the initial amorphous layer thickness on the crystallization velocity within the near-surface region, the crystallization velocity of Si was measured for initial thicknesses of ~400–1200 nm. Over the depth range of interest, 90–280 nm, both the crystallization velocity and activation energy for crystallization were found to be independent of the initial amorphous layer thickness.

The crystallization velocities measured for Si, Ge, and a range of alloy layers are shown as a function of reciprocal temperature in Fig. 2. Also shown for each sample is a curve fit, $v = v_0 \exp(-E_a/kT)$, where v_0 is the preexponential factor and E_a is the activation energy; an excellent fit to the data is achieved for all samples. The extracted preexponential factors and activation energies are listed in Table I. It should be noted that two sets of data are shown for the $Si_{0.79}Ge_{0.21}$ alloy, one for an amorphous layer produced in as-grown materials and one for the layer preannealed at 1100 °C before amorphization. If this layer contained a high level of residual strain as-grown and if this strain was sufficient to affect the crystallization velocity, then the high-temperature anneal, which is sufficient to induce strain relief, would be expected to alter the

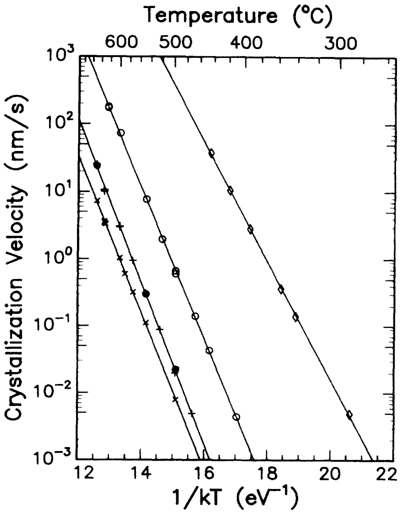

FIG. 2. Arrhenius plots of the crystallization velocity for four different strain-relaxed alloy layers: Si (×), $Si_{0.79}Ge_{0.21}$ (+), $Si_{0.47}Ge_{0.53}$ (○), and Ge (◇). For the $Si_{0.79}Ge_{0.21}$ alloy, the velocity from the SiGe alloy preannealed at 1100 °C for 60 s is also shown (•).

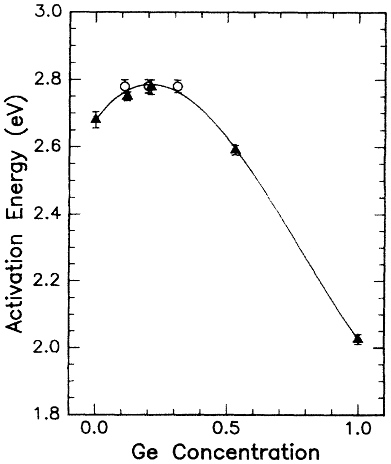

FIG. 3. Activation energy for solid-phase epitaxial crystallization as a function of Ge concentration. The closed symbols refer to strain-relaxed alloy layers grown by MBE whereas the open symbols refer to similar layers grown by CVD. The solid line is included as a guide to the eye.

crystallization kinetics. As shown in Table I both the absolute crystallization velocity and activation energy are identical for the as-grown and annealed samples. This implies that, if present, residual strain does not influence the crystallization kinetics significantly.

Interestingly, Table I shows that the activation energy for SPEC does not vary monotonically between the values for Si and Ge, but increases above that of Si for low Ge contents. This is more clearly seen in Fig. 3 which plots the measured activation energy as a function of Ge composition. Similar results have been observed for thin (100 nm) SiGe layers strain relaxed by high-temperature annealing [21]. The high concentration of strain relieving defects present in such layers appears to have little effect on the results. Shiryaev, Fyhn, and Nylansted-Larsen [22] have also reported an activation energy higher than that of Si for a strain-relaxed alloy with $x = 0.25$, although in this case the reported difference was well within the experimental error range. High activation energies have also been reported for SPEC in SiGe strained layers but, as mentioned in the introduction, such measurements are complicated by the changing mode of crystallization accompanying strain relief.

The observed increase in activation energy is difficult to understand on the basis of existing SPEC models. From the viewpoint of bond-breaking models the activation energy might reasonably be expected to vary monotonically between that of Si and Ge since both the Si-Ge and Ge-Ge bond strengths are less than that of Si-Si [23]. In general, however, the activation energy for SPEC is considered to be made of two components, a defect formation energy (bond breaking) and a defect migration energy (reorientation of atoms at the interface). Since the formation energy is expected to decrease with increasing Ge content, it must be concluded that the observed increase in activation energy results from the defect migration energy, perhaps as a consequence of the local strain associated with the incorporation of a Ge atom into the crystal lattice. This is necessarily a fairly general conclusion but a more detailed explanation requires a more complete understanding of the atomistic processes responsible for SPEC. In this regard, it would be of considerable interest to study the concentration dependence of the activation energy for Ge rich alloys (i.e., $x \sim 0.9$).

TABLE I. Activation energy and preexponential factor from Arrhenius fits to the crystallization velocity data. The uncertainties given are the statistical uncertainties only. The value given for $Si_{0.79}Ge_{0.21}$ is based on both values with and without the preanneal. The activation energy and preexponential factor is 2.78 eV and 3.6 × 10^9 cm/s for the samples without and 2.78 eV and 3.5 × 10^9 cm/s for the samples with preanneal.

	x							
	0	0.11	0.12	0.20	0.21	0.31	0.53	1.00
E_a (eV)	2.68 ± 0.024	2.78 ± 0.02	2.75 ± 0.013	2.78 ± 0.02	2.78 ± 0.022	2.78 ± 0.02	2.59 ± 0.015	2.02 ± 0.015
v_0 (10^9 cm/s)	0.31 ± 0.1	2.3 ± 0.6	1.3 ± 0.2	3.3 ± 0.9	3.6 ± 1.1	6.5 ± 1.7	6.4 ± 1.4	0.61 ± 0.16

The above discussion is predicated on the assumption that SPEC is thermally activated with a well defined activation energy. However, Aziz [24] has recently shown that even the best available velocity data [2] can be well described by an alternative two-stage mechanism. In particular, he has demonstrated that the data can be adequately described by a mechanism consisting of two processes in series, each of which is rate limiting, and having activation energies differing by <0.5 eV. (As an example of such a process, Aziz suggested a model in which dangling bonds are first transported to the interface from the bulk and then undergo an interfacial reaction.) If such a two-stage (or multistage) process is responsible for SPEC, then activation energies have little real meaning.

In conclusion, solid-phase epitaxial crystallization kinetics were measured for Si, Ge, and a range of strain-relaxed SiGe alloy layers. The activation energy for crystallization was shown not to decrease monotonically from the Si value to the Ge value with increasing Ge concentration but to increase above that of Si for Ge concentrations <0.4. The maximum activation energy was ~ 0.1 eV above that of Si and was observed for alloy compositions of approximately $x = 0.2$. This result was discussed in terms of existing bond-breaking models of crystallization.

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