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TIME-RESOLVED REFLECTIVITY MEASUREMENT
OF THE PRESSURE-ENHANCED CRYSTALLIZATION RATE OF AMORPHOUS Si IN A
DIAMOND ANVIL CELL.

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ABSTRACT

We have measured the pressure dependence of the solid phase epitaxial growth (SPEG) rate of self-implanted Si (100) by using the in-situ time-resolved reflectivity technique [1] in a high-temperature and high-pressure diamond anvil cell (DAC). With fluid argon as the pressure transmission medium, a clean and perfectly hydrostatic pressure environment is achieved around the sample. The external heating geometry employed in the DAC provides a uniform temperature across the sample. At temperatures in the range of 530 - 550 °C and pressure up to 50 kbars (5 GPa), the growth rate is enhanced by up to a factor of ten over that at 1 atmosphere pressure. The results are characterized by a negative activation volume of approximately $-3.0 \text{ cm}^3/\text{mole}$ (-27% of the atomic volume). These preliminary results show a significantly weaker pressure dependence than does the previous work of Nygren *et al.* [2], who found an activation volume of $-8.7 \text{ cm}^3/\text{mole}$. The implications of these results for the nature of the defect responsible for thermal SPEG and irradiation enhanced SPEG is discussed.

INTRODUCTION

The solid phase epitaxial growth (SPEG) of amorphous silicon produced by ion implantation has been extensively studied at ambient pressure and its kinetics are fairly well established [1]. In addition, there are two published works on the pressure dependence of SPEG in silicon. Nygren *et al.* [2] measured the SPEG rate of self-implanted silicon $\langle 100 \rangle$ at pressures up to 20 kbars (2 GPa) in a piston-cylinder pressure apparatus with solid NaCl as a pressure transmission medium. They found a pressure-enhanced SPEG rate, characterized by a negative activation volume of -70% of the atomic volume, similar to the negative activation volume found by Fratello *et al.* [3] for the growth of quartz from fused silica. Vasin *et al.* [4] implanted Si (111) with an unreported species and observed SPEG at low pressures (0-300 bars) in a gas apparatus. They reported a very slight retardation in the rate, i.e., a positive activation volume.

In both of the high pressure works above, the high-pressure annealing treatment was performed separately from the determination of growth velocity. In the former [2], the growth velocity was measured using Rutherford backscattering and channeling techniques, while in the latter [4], the growth velocity was obtained from sheet resistivity measurements. Recently, Licoppe *et al.* [5] used the *in situ* time resolved reflectivity (TRR) technique, developed by Olson *et al.* [6], to observe a pressure-enhanced SPEG rate of GaAs in a gas apparatus at pressures of up to 5 kbars. The *in situ* technique has several advantages over the post-mortem measurements performed previously. Instantaneous measurements of the growth rate eliminate the need for assumptions about its time-dependence; they also eliminate sample-to-sample variations by allowing growth rates under varying conditions to be measured on the same sample.

In this work, we have performed TRR measurements of the SPEG rate in self-implanted Si $\langle 100 \rangle$ in a high-temperature and high-pressure diamond anvil cell (DAC), which can attain pressures of hundreds of kilobars. Fluid argon, loaded cryogenically, is used as the pressure transmission medium to ensure a clean and perfectly hydrostatic environment around the sample.

EXPERIMENT

A wafer of Si (100) (p-type, 1-2 $\Omega\text{-cm}$) was polished on both sides to a thickness of 25-40 μm and implanted on both sides at 77 K with $^{30}\text{Si}^+$ (each side at 180 keV, $2 \times 10^{15}/\text{cm}^2$, 0.4 $\mu\text{A}/\text{cm}^2$; and at 60 keV, $1 \times 10^{15}/\text{cm}^2$, 0.4 $\mu\text{A}/\text{cm}^2$). The implantation procedure produced an amorphous

layer approximately 3000 Å thick. The wafer was then cut into many 200 μm x 200 μm square samples.

The diamond anvil cell used in this study is designed after the Piermarini-Block cell [7] with added external heating geometry. In Fig. 1 we show a schematic of the pressure chamber. The pressure is applied with a 0.7 mm diameter surface of each diamond anvil. Metal gaskets were made out of 10 mil (254 μm) thick Inconel x750 sheet. The gaskets were preindented with the diamonds; holes of about 350 μm in diameter were subsequently drilled in the center of the indentation. After placing the silicon sample and several small (5-10 μm) ruby chips into the gasket hole, the cell was cooled to liquid nitrogen temperature while gaseous argon flowed across the diamonds. The chamber was sealed after a sufficient quantity of liquid argon condensed to fill it.

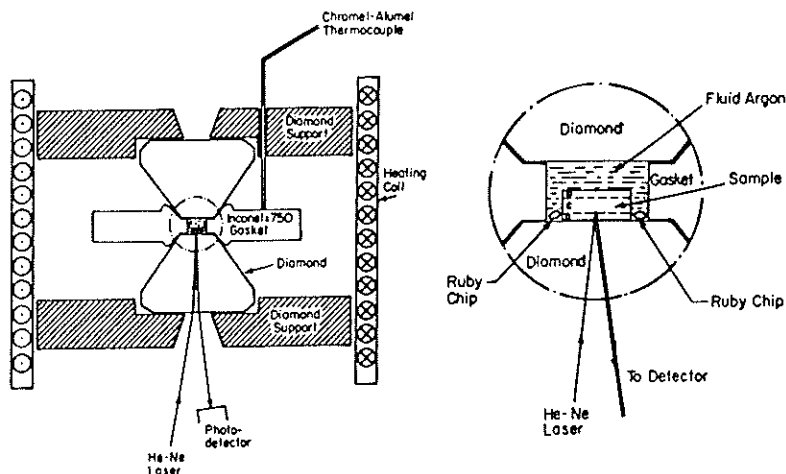


Fig. 1. Schematic of the pressure chamber of the high-temperature and high-pressure diamond anvil cell.

The ruby fluorescence technique [8], which measures the pressure-induced shifts of the ruby fluorescence lines (692.7 nm and 694.2 nm) excited by an argon ion laser, was used to measure the pressure on the sample.

The cell was heated by using resistive heating coils. A chromel-alumel thermocouple, placed next to the diamond and in contact with the gasket, was used to monitor the temperature. During the course of an annealing run, temperature stability of $\pm 0.5^\circ\text{C}$ was maintained. TRR signals from a HeNe laser ($\lambda = 693 \text{ nm}$) focussed on the sample were detected with a photodetector and recorded onto a chart recorder.

RESULTS AND DISCUSSION

In Table I we list the runs and the resulting growth velocities. The ambient pressure runs were done in the DAC in air (no argon loading); the growth velocities obtained with this method are in good agreement with published values for similar materials.[2] In Fig. 2(a) we show the TRR signal at ambient pressure and 550°C. The distance between two reflectivity maxima corresponds to the interface traversing a distance of 652 Å; hence, this crystal grew at a rate of 0.35 Å/sec. In Fig. 2(b) we show the TRR signal at 530°C and 50±5 kbars. Despite the lower temperature compared to Fig. 2(a), this crystal grew at almost twice the rate.

Table I: conditions and results of high pressure runs

Run #	Temperature (°C)	Pressure (kbars)	Velocity (Å/sec)
1	566	Ambient	1.0
2	550	Ambient	0.35
3	550	27±5	1.284
4	550	Ambient	0.37
5	540	Ambient	0.140
6	530	50±5	0.667

Assuming crystal growth to be a simple thermally-activated process, the growth rate is expressed phenomenologically by:

$$v = v_0(T) \exp(-P\Delta V^*/RT), \quad (1)$$

where ΔV^* , the activation volume of the SPEG process, can be found from the slope of the $\ln v$ vs P plot. Within the context of transition state theory, ΔV^* is the volume of the transition state minus the volume of the initial state. In Fig. 3 we plot the pressure dependence of the SPEG rates at 550°C and 530°C from the data in Table I. The ambient pressure velocity at 530°C was extrapolated from the three measured ambient pressure velocities, and is in reasonable agreement with published values. The activation volume, ΔV^* is found to be approximately -3.0 ± 0.5 cm³/mol, which is about 27% of the atomic volume of crystalline silicon (12 cm³/mol).

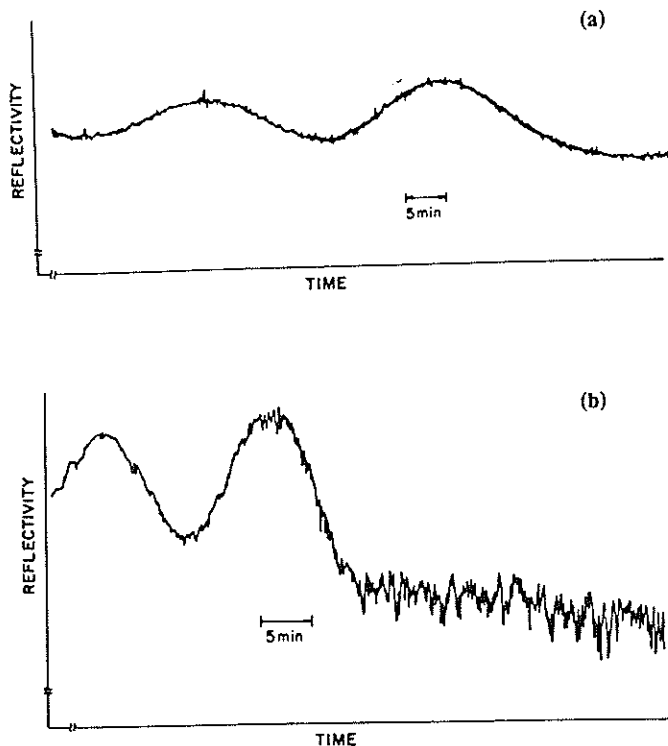


Fig. 2. (a) TRR signal at ambient pressure and 550°C. The SPEG velocity was 0.35 Å/sec. (b) TRR signal at 50 kbars and 530°C. The SPEG velocity was 0.667 Å/sec.

The activation volume is negative, which means phenomenologically that the population of a lower-volume transition state is increased, relative to that of the starting state, by the application of pressure. This finding is in qualitative but not quantitative agreement with that of Nygren *et al.*, who found an activation volume of approximately 70% of the molar volume for the same process. Ours is a significantly weaker pressure dependence. It is possible that nonhydrostatic stresses in the previous experiment affected the results.

The ruby fluorescence technique for pressure measurement is very simple and can be very accurate. However, the accuracy was not optimized during these preliminary experiments, and we estimate an uncertainty of ± 5 kbars in the pressure measurements. Because at high temperatures ($>300^\circ\text{C}$), the ruby lines broaden to such an extent that the determination of the fluorescence peak positions becomes impossible, the pressure on the sample was measured at room temperature. The pressure was measured twice, once before the annealing run and once after. Through proper calibration techniques, we should be able to determine the pressure at elevated temperature and its relation to that measured at ambient temperature. At this point, we believe that the difference is small, and that the pressure at high temperature could be slightly lower than the one measured at room temperature. This judgement is based on the fact that the Belleville spring washers, which are used to produce the force on the diamonds, were slightly heated (to about 80°C) during the anneal, which could lead to a slight decrease in the spring constant of the washers and a lower pressure. In addition, the difference in thermal expansion between the argon pressure medium and the gasket material may lead to a change in pressure with temperature, even if the load on the diamond anvils is kept constant.

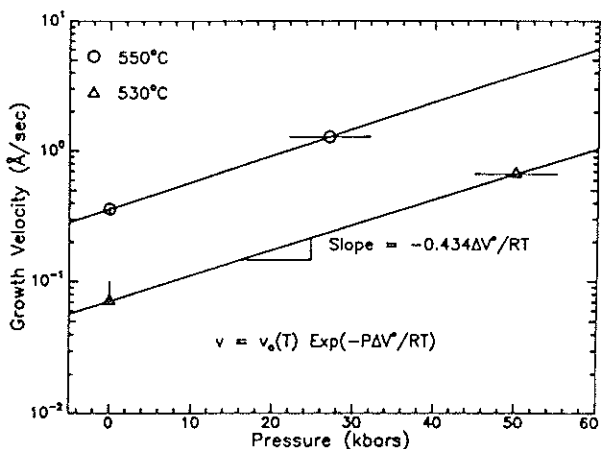


Fig. 3. Growth rate vs pressure at 530°C and 550°C . The activation volume is approximately $-3.0 \pm 0.5 \text{ cm}^3/\text{mole}$.

The 652 \AA peak-to-peak distance of the TRR signal used to calculate the SPEG velocities is equal to $\lambda/2n$, where n is the index of refraction of amorphous Si at this wavelength. Since n in general depends on the pressure, the SPEG velocities calculated from the TRR signals should take this effect into account. We have observed the total times needed to completely crystallize the amorphous Si layer at 550°C at ambient and at 27 kbars. We have found that the time ratio matches the inverse of the indicated velocity ratio. Hence the effect of pressure on the index of refraction is negligible.

There is a considerable amount of recent work relevant to the nature of the atomic defects responsible for SPEG [9-15]. Recent experiments in irradiation enhanced SPEG have established a temperature dependence of approximately 0.3 eV for this process [14,15]. This number has been associated with the activation energy for migration of a SPEG defect. Assuming that there is a single type of defect controlling both thermal SPEG and irradiation enhanced SPEG, whose migration to the boundary is the rate-limiting step in ion-induced SPEG, an exponentially pressure-enhanced growth rate can be used to place an upper limit on ΔV_f , the formation volume of such a defect. A lower limit of -50 % of Ω_a , the atomic volume, is obtained for ΔV_m , the migration volume, by realizing that the PV term in the free energy barrier to migration cannot reduce it to zero without being reflected in a break in the pressure-dependence data. In our work, the overall activation volume, which is the sum of ΔV_f and ΔV_m , is -27 % of Ω_a . Hence ΔV_f cannot be greater than +0.23 Ω_a . It is very unlikely that this defect could be a vacancy because this number, percentage-wise, is much smaller than the 70 % of the atomic volume estimated by Scholz and Seeger [16] for the vacancy volume in germanium, for which they took into account the lattice relaxation around the vacant site. Since Si is more tightly bound than Ge, one might expect that in Si the relaxation around the vacant site could be less, leading to a larger percentage of Ω_a for the vacancy volume. If subsequent experiments establish an exponentially increasing pressure-dependence to yet greater pressures, the maximum possible value of ΔV_f will be pushed further down.

CONCLUSIONS

We have measured the pressure dependence of the solid phase epitaxial growth rate of self-implanted Si (100) by using the in-situ time-resolved reflectivity technique in a high-temperature and high-pressure diamond anvil cell (DAC). At temperatures in the range of 530 - 550 °C and pressure up to 50 kbars (5 GPa), the growth rate is enhanced by hydrostatic pressure and is characterized by a negative activation volume of approximately -3.0 cm³/mole (-27% of the atomic volume). We find a somewhat weaker pressure dependence than was found by Nygren *et al.* in earlier work. If these preliminary data are substantiated by more thorough studies now in progress, we can draw the following conclusion concerning the nature of the defect controlling SPEG: if there is a single type of SPEG defect in both thermal SPEG and irradiation enhanced SPEG, whose migration to the boundary is the rate-limiting step in ion-induced SPEG, then its volume is no greater than 23 % of the molar volume of crystalline Si.

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