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# Solid Phase Recrystallization of Amorphous and MBE-Grown Ge Films on Si Substrates by Annealing under Ultrahigh Pressure

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A novel method for reducing the thermal mismatch problem in heteroepitaxy is presented. In this method, an amorphous film deposited on a dissimilar single crystalline substrate is crystallized in solid phase by annealing under ultrahigh pressure (UHP), or an epitaxial film grown by MBE or CVD is annealed under UHP for rearranging the interface bonding. Then, both temperature and pressure are simultaneously decreased in such a way that the effective thermal expansion coefficient modified by elastic strain of the film is equal to that of the substrate. Validity of the method has experimentally been shown using Ge-on-Si structures.

## 1. Introduction.

Heteroepitaxy of dissimilar materials has been known to be important in fabrication of future electronic and optical devices. However, crystalline quality of these films is not yet perfect due to large lattice and thermal mismatches between the films and the substrates. In this paper, we propose a novel method to solve the problem of thermal mismatch based on a general property of materials that, soft materials possess relatively large thermal expansion coefficients, and validity of the method is investigated using Ge-on-Si structures.

## 2. Theoretical Consideration.

The original idea of this method is depicted in Fig.1. In this figure, the thermal expansion coefficient ( $\alpha$ ) and the elastic strain ( $\varepsilon$ ) of the film are assumed to be larger than those of the substrate. When the film is stuck to the substrate under atmospheric pressure (AP), the sample bends downwards with decrease of temperature, as shown in Fig.1(a). On the other hand, when the film is stuck under ultrahigh pressure (UHP) as in Fig.1(b), the sample bends either downwards with decreasing temperature or upwards with decreasing pressure. Therefore, we expect a state of strain-free where the sample bends neither upwards nor downwards by decreasing both temperature and pressure simultaneously. This state is achieved when the effective thermal expansion coefficient of the film which is defined as $\alpha - \varepsilon / \delta T$ ( $\delta T$: temperature difference), is equal to that of the substrate. As a linear approximation, the relations for Ge/Si and GaAs/Si are deduced to be $P=3.0\ \delta T$ and $P=4.2\ \delta T$ (P:MPa and $\delta T$: ℃ ), respectively.[1]

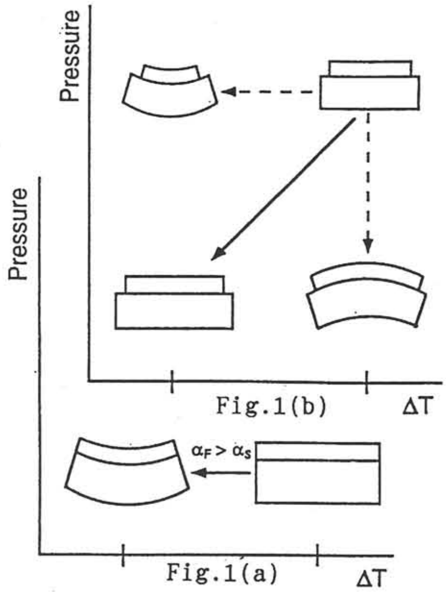


Fig.1 Explanation of strain-free growth using bimetal model.

## 3. Experimental Approach.

In the experiment, a piston-cylinder type of ultrahigh pressure apparatus which can generate pressure up to 2.1GPa (21kbar) illustrated in Fig. 2 was used. The cylinder was filled with Ar gas which was used as a pressure transmission medium. An electric furnace with heating range up to 800 ℃ was placed in the cylinder. To minimize temperature fluctuation during annealing, the samples of typical size of 2x3mm² were enclosed in a copper tube about 5mm in diameter before inserting into the furnace. Temperature in the copper tube was monitored by a thermocouple which was controlled within ± 1 ℃ under UHP by a thyristor-controlled power supply.

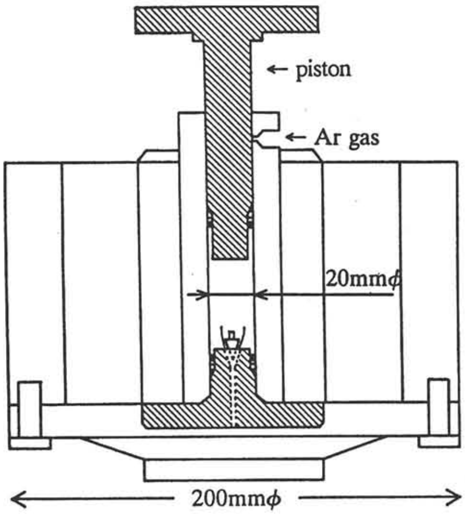


Fig.2 Schematic of the piston-cylinder apparatus.

In samples preparation, substrates were cleaned by Shiraki method. The amorphous Ge films were deposited on Si(100) substrates by vacuum deposition near room temperature and were recrystallized by solid phase epitaxy (SPE) at 400 ℃ for 30 min under atmospheric pressure as well as various UHP. Ge films were also grown on Si(111) substrates using molecular beam epitaxy (MBE) and the samples were annealed at 350 ℃ under various UHP. The crystalline quality of the Ge films was characterized by Rutherford backscattering spectroscopy (RBS), while the residual strain of the films was measured by both laser Raman spectroscopy and X-ray diffraction analysis.

## 4. Results and Discussion.

Several results are compiled and discussed as follows:

4.1 Fig.3 shows the Raman spectra of the SPE samples annealed at 400 ℃ for 30 min at AP and 1.14GPa. The spectrum for bulk Ge is also shown for comparison. We can see from Fig.3 that the tensile strain in the Ge film at UHP is about 1/3 of the AP-annealed sample. Almost the same results were obtained from the X-ray diffraction analysis. It was found in many SPE samples that the residual strain in the Ge films became about 1/3 of the AP-annealed samples when they were annealed at 1.14GPa. The results are summarized in Fig.4.

4.2 Samples from the same original deposited film were annealed seprately at AP, 1.14GPa and 2.1GPa at 400 ℃ for 30 min.

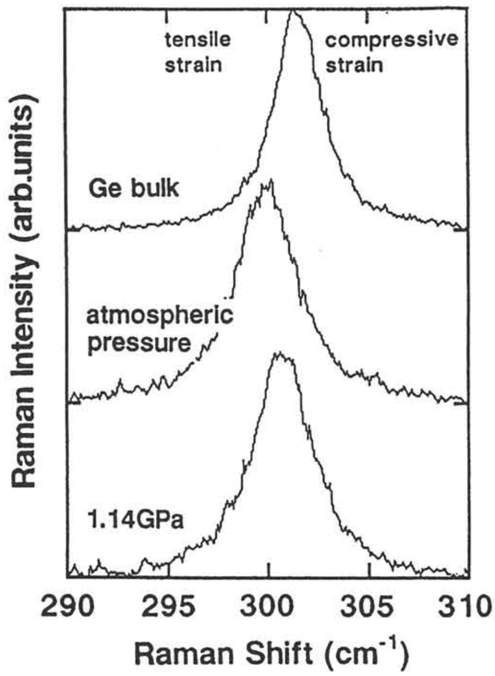


Fig.3 Raman spectra of Ge(160nm)/Si(100) sample recrystallized by SPE.

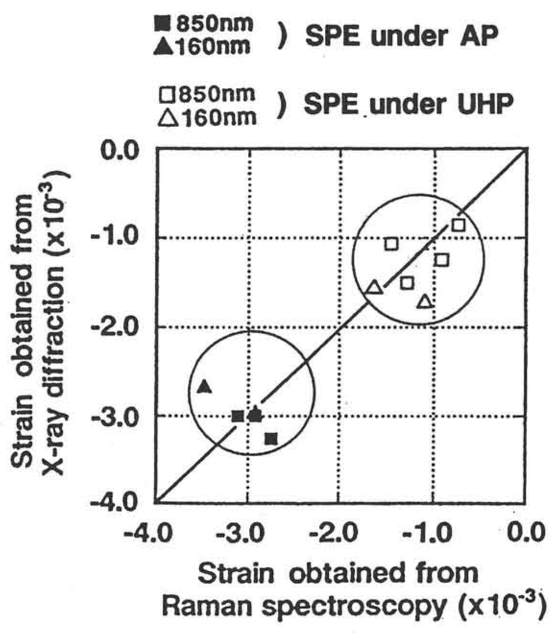


Fig.4 Measurements between Raman spectroscopy and X-ray diffraction analysis agree to one another.

The crystalline quality of these samples were characterized by RBS. The channeling minimum yields $\chi_{min}$ of these samples were almost the same (about 11%) as shown in Fig.5, which indicates that degradation of the crystalline quality by the UHP annealing process is negligible at least in these samples.

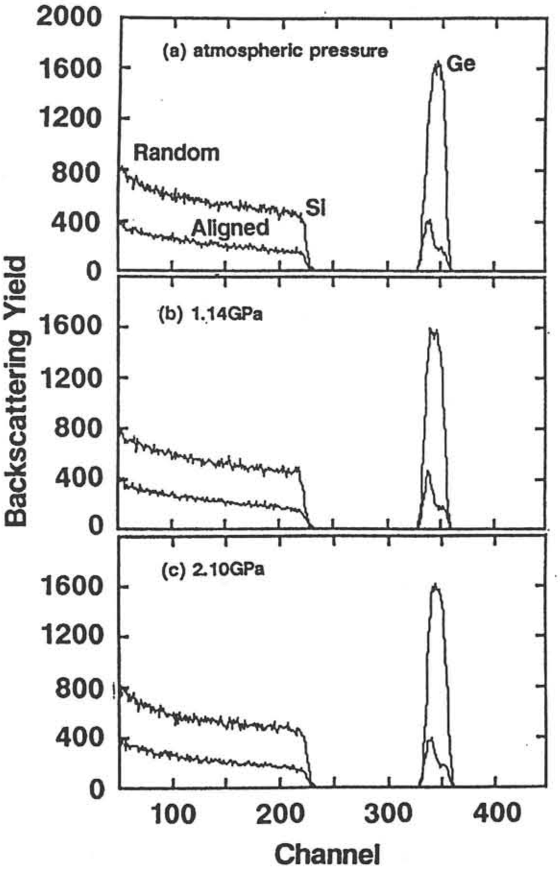


Fig.5 RBS spectra for Ge/Si(100) formed by SPE at 400 ℃ for 30 min. at AP, 1.14GPa and 2.1GPa.

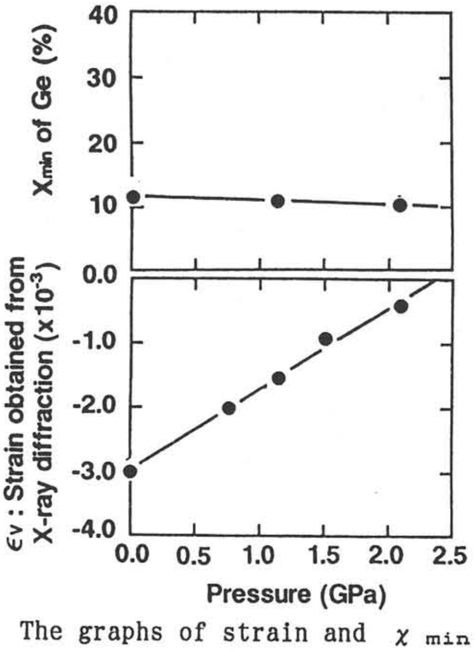


Fig.6 The graphs of strain and $\chi_{min}$ vs pressure in Ge(160nm)/Si(100).

4.3 Variation of the residual strain and $\chi_{min}$ with pressure in the SPE samples is plotted in Fig.6. It is clear that residual strain in the film decreases linearly with increase of pressure while the crystalline quality is almost maintained.

4.4 Similar experiments were carried out for MBE-grown Ge films. However, the residual strain in the as-grown films is relatively small as shown in the Raman spectra in Fig.7. More precise measurements of the strain are currently being attempted.

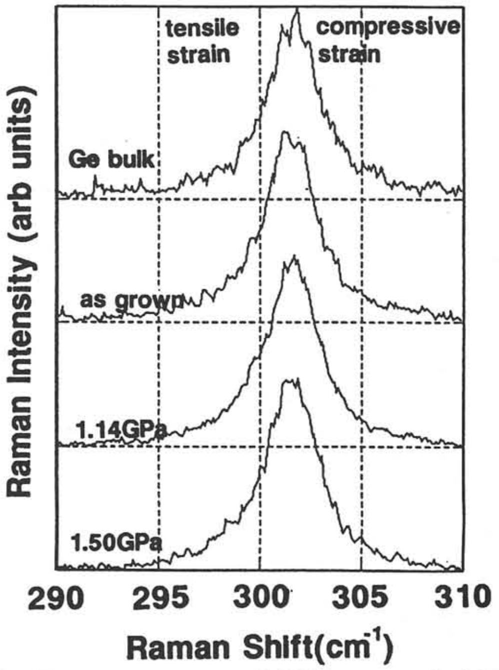


Fig.7 Raman spectra of MBE-grown Ge(1600nm)/ Si(111) samples recrystallized at 1.14GPa and 1.50GPa, as well as those of bulk and as-grown sample.

## 5. Conclusion.

We proposed a novel method to solve the thermal mismatch problem in heteroepitaxial growth. It was found that the residual strain in Ge films on Si(100) substrates was linearly decreased with increase of the pressure during annealing, while the crystalline quality was kept constant. We conclude from these findings that the solid phase recrystallization method in ultrahigh pressure is particularly effective in fabricating strain-free heterostructures.

## Reference.


1) H.Ishiwara, T.Sato and A.Sawaoka; Mat. Res. Soc. Symp. Proc. Vol. 239. (in press).