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Growth mechanisms in thin film epitaxy of Si/SiGe from hydrides

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Abstract

Epitaxial growth of Si/SiGe from hydride precursors has been well established as the preferred technique for preparation of 'virtual substrate' and active layers of heterojunction metal-oxide-semiconductor devices as well as other Si/SiGe heterojunction based device structures. This paper reviews briefly the role of hydrogen in the growth mechanisms and establishes the basic reaction pathways in the growth process. The surface related segregation of Ge and As are examined in the context of formation of sharp SiGe/Si heterojunctions and sharp doping profiles. The influence of the growth environment on these surface segregation processes are revealed by the extended rate equation based 'two-site' exchange model. The optimisation of growth conditions are clearly identified from the trend gathered from secondary ion mass spectrometry measurements. The strain relaxation process during the growth of virtual substrates often leads to bunching and a high density of threading dislocations and requires substantially thicker grading layers. Some preliminary work shows that incorporation of 'stresser' layers in the grading region substantially reduces these detrimental features enabling relatively thin grading layers to be used. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Epitaxial; Hydride; Heterojunction

1. Introduction

Thin film epitaxy is an essential tool for producing heterojunction based structures for microelectronic and optoelectronic applications. For the Si/SiGe material system, growth from hydride precursors using chemical vapour deposition (CVD) or Gas Source Molecular Beam Epitaxy (GSMBE) have been the favoured techniques due to their dominance in the microelectronic industry, as well as their sustained operation without breaking vacuum of the growth system. Compared with the Solid Source MBE counterpart, the chemistry of the hydride pyrolysis reactions are complicated but there are substantial advantages on the segregation of matrix element Ge and group V dopants as well as other issues which make CVD and GSMBE preferable. This paper reviews briefly the role of hydrogen in controlling the overall reaction/growth rate and reports on some recent findings more applicable in the GSMBE environment at high temperatures. The surface segregation of Ge and As are examined in detail using a refined 'two site exchange' model and the trend in their dependence on growth parameters are revealed through secondary ion mass spectroscopy (SIMS) depth profiles as well as the solution of rate equations in the phenomenological model. The growth of a graded virtual substrate has been the main route towards a $Si_{1-x}Ge_x$ substrate, essential in the band structure engineering utilising strain induced changes in this material system. The strain relaxation processes cause an increase in the threading dislocation density as well as bunching of threading dislocations [1]. Some preliminary result have indicated that insertion of additional high stress layers in the grading region substantially reduce the threading dislocation count and appear to be more effective compared with their counterpart in the constant composition region. This can potentially reduce the thickness of the virtual substrate while achieving a similar dislocation density to their conventional counterpart.

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2. Kinetics of the pyrolysis reactions

Hydrogen has long been recognised as having an important role in controlling the pyrolysis reaction of hydrides on Si(001) surfaces [2–4] and the growth rate of Si or SiGe. It is a reaction product of the pyrolysis of hydride precursors such as silane, disilane or germane and passivates potential adsorption site by saturating the dangling bond available on the Si(001) surface. The steady state growth rate under a particular growth condition is determined by the balance of hydrogen generation by the pyrolysis processes and the desorption of hydrogen as H_2 molecules. The growth rate is, therefore, limited by the rate of desorption of molecular hydrogen at the steady state hydrogen coverage. This steady state condition has been modelled using rate equations in a number of publications [5,6].

The rate equation based models rely on the knowledge of reaction pathway, and assumes the hydrogen from hydride precursors evolves into monohydride before desorbing as hydrogen molecules. While a consensus exists in the community on the reaction pathway, the confirmation of the dominance of this hydrogen desorption pathway over other possible alternatives only came about as a result of combination of experimental techniques [7]. Using Temperature Programmed Desorption (TPD), Reflection High Energy Electron Diffraction (RHEED) and ex-situ X-ray rocking curve measurements of layers grown using temperature cycled growth, it was shown that one third of a monolayer of Si is deposited each time a clean surface is saturated by disliane adsorption at temperatures in excess of 400 °C. The result is clearly consistent with sequential reduction of the hydride into the monohydride form prior to desorption of molecular hydrogen.

Rate equation models are often compared with experimental data [8] obtained using RHEED intensity oscillation technique [9]. The data is only available over a limited temperature range and the fitting sometime leads to an activation barrier of 1.8 eV associated with the desorption barrier to hydrogen. This value is, however, consistently smaller than those obtained from TPD measurements of hydrogen desorption studies. Using thickness measurements similar to those described in [7], growth rate over a much larger range are obtained [10] and are shown as an Arrhrenus plot in Fig. 1. A value of 2.2 eV is obtained using the standard model, in close agreement with TPD measurements. However, the data shown in Fig. 1 revealed two points which are at odds with the current understanding.

In the low temperature regime, the growth rate shows a weak disilane incident flux dependence. Given that the surface is passivated by hydrogen with almost full coverage, additional flux dependent mechanism of hy-

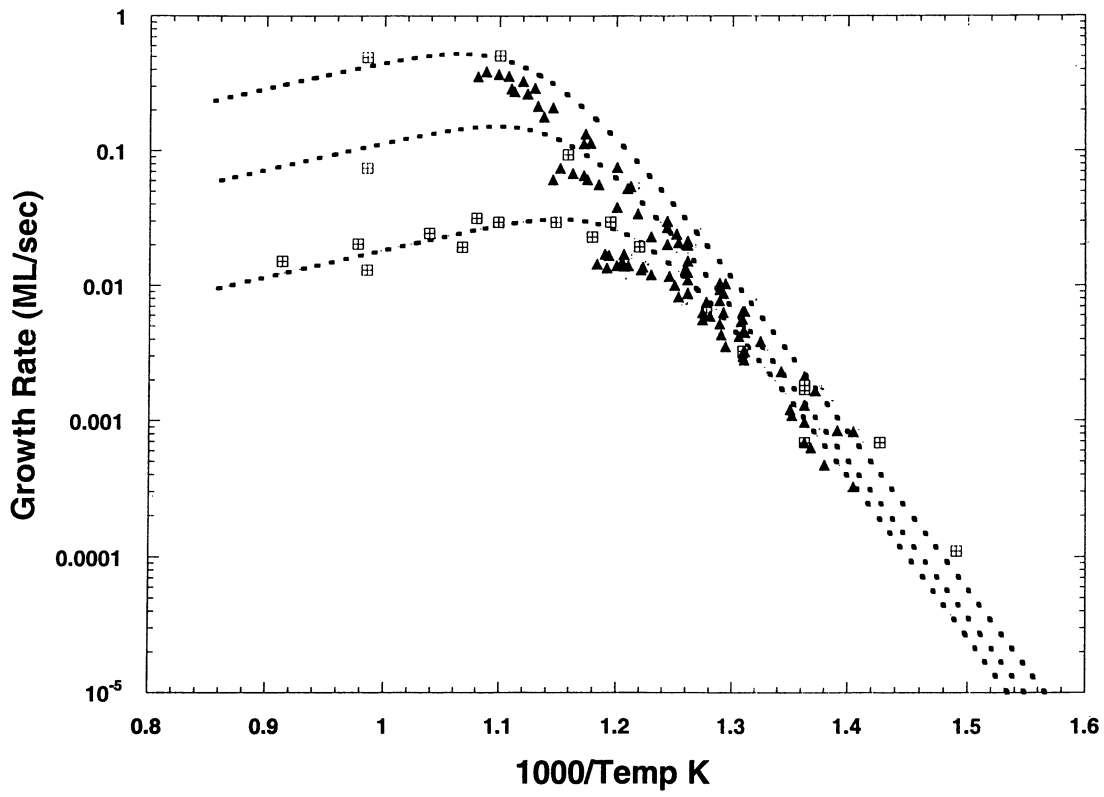


Fig. 1. Growth rate of silicon on the Si(001) surface as a function of temperature. Solid symbols show results obtained from RHEED intensity oscillation whereas open symbols correspond to results obtained from ex-situ X-ray diffraction measurements. The three lines are derived from results based on three different incident disilane fluxes.

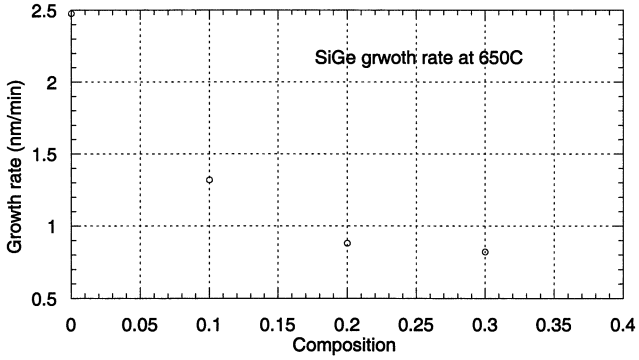


Fig. 2. Growth rate of SiGe as a function of Ge fraction at 650 °C using GSMBE. The disilane incident flux is fixed while germane flux was changed. The results were obtained using ex-situ X-ray diffraction measurements.

drogen removal have to be present. It has been suggested that hydrogen abstraction may be responsible [10,11] but this mechanism has to be temperature dependent with essentially the same activation barrier of 2.2 eV.

The growth rate at high temperature is generally thought to be temperature independent and limited only by the supply rate of the hydride precursors. The data shown in Fig. 1 clearly indicates to the contrary. In this high temperature regime, the growth rate decreases with increasing temperature suggesting that either the trapping probability of the incident hydride precursors is reduced or that some intermediate reaction product is desorbing from the surface (the substrate temperature is still too low for evaporation of elemental Si).

The growth of SiGe alloy films further complicates the issue. The presence of Ge modifies the hydrogen desorption processes and hence changes the growth rate. While it is generally recognised that presence of Ge enhances the hydrogen desorption and increases the growth rate at low temperatures [12,13], its effect at high temperature is quite the opposite. Fig. 2 shows the SiGe homo-epitaxy growth rate at 650 °C as a function of the alloy composition obtained with the same disilane incident flux and different germane fluxes. It is clear from Fig. 2 that the presence of higher Ge concentration at the surface reduces the growth rate and the hydrogen desorption is clearly not the rate limiting process controlling the overall growth rate under these circumstances. Consistent with the growth of Si at high temperatures under GSMBE conditions (as shown in Fig. 1), the sticking coefficient of the hydride on a surface with a higher Ge concentration is lowered in comparison to clean Si surfaces as temperature increases and hence becomes the rate controlling step in the overall reaction.

The growth of Si/SiGe from hydride under CVD or its ultra low pressure variant [14] is less susceptible to this problem. The larger incident flux maintains a high hydrogen coverage and the growth rate remains to be controlled by the desorption of molecular hydrogen. Under these conditions, the main effect of the presence of Ge is still the enhancement of desorption rate leading to growth rate enhancement.

3. Surface segregation of Ge and As

Surface segregation during epitaxial growth refers to the preference of a matrix element of a random alloy, or an impurity such as a dopant, to reside on the surface rather than in the bulk. This is a surface related process, and is not the same as concentration gradient driven diffusion process. Indeed, the surface concentration is generally higher than the concentration in the bulk of the crystal. The atomistic picture of the surface segregation process is not very clear but a surface site versus bulk site phenomenological models have been developed to provide some understanding on how the processes may be influenced by external parameters such as temperature. In this two-sites exchange model, the surface site and bulk site are given certain binding energies and a barrier exists between the two. The original models [15,16] are extended to incorporate the growth rate directly [17] with the final rate equation given by:

$$\frac{\mathrm{d}n_\mathrm{s}}{\mathrm{d}x} = \frac{1}{\beta}k_+ n_\mathrm{b}\left(1-\frac{n_\mathrm{s}}{N}\right) - \frac{1}{\beta}k_- n_\mathrm{s}\left(1-\frac{n_\mathrm{b}}{N}\right) - \frac{n_\mathrm{s}}{a}$$
$$\frac{\mathrm{d}n_\mathrm{b}}{\mathrm{d}x} = -\frac{1}{\beta}k_+ n_\mathrm{b}\left(1-\frac{n_\mathrm{s}}{N}\right) + \frac{1}{\beta}k_- n_\mathrm{s}\left(1-\frac{n_\mathrm{b}}{N}\right) + \frac{n_\mathrm{s}}{a} - \frac{n_\mathrm{b}}{a} \quad (1)$$

where n_s, n_b are surface and bulk concentrations, x is the growth front position from a fixed reference, β is the growth rate, k_+, k_- are rate constants and a is the monolayer thickness. This facilitates the analytical solutions of the rate equations in the dilute regime with solution of surface and bulk concentrations showing two characteristic decay length given by:

$$\lambda_1 = \frac{2\beta a}{2\beta + a(k_+ + k_-) + \sqrt{a^2(k_+ + k_-)^2 + 4ak_+\beta}}$$
$$\lambda_2 = \frac{2\beta a}{2\beta + a(k_+ + k_-) - \sqrt{a^2(k_+ + k_-)^2 + 4ak_+\beta}} \quad (2)$$

In the equilibrium regime where the growth rate approaches zero, the first decay length approaches zero where as the second decay length is determined by the Gibb's energy of segregation [18] as below:

$$\lim_{\beta\to 0}\ \lambda_2 = a\left(1+\frac{k_+^0}{k_-^0}\mathrm{e}^{-\Delta G/kT}\right) \quad (3)$$

However, the SIMS observation of Ge concentration in Si capping layers suggest that the decay length increases with temperature and, therefore, surface segregation of Ge during GSMBE growth occurs generally well away from the equilibrium regime and is limited by kinetic barriers.

The kinetic limited regime can be identified by the condition of $\beta \to \infty$ and both decay lengths have a limiting value equal to a. This represents the smallest possible decay length within the model and would be the optimised condition in controlling the segregation processes. It is, however, clear that a larger growth rate will lead to a smaller decay length and increase growth rate is clearly desirable (at a given temperature) for reducing the segregation process. Fig. 3 shows Ge concentration profiles in Si capping layers becoming wider as the growth rate is decreased (as indicated by source pressure) in comparison with a sample grown at the same temperature but with the highest growth rate employed (3 Torr source pressure). The difference in the sharpness of the decay profile is evident as the slower growth rate (0.3 Torr source pressure) gives rise to the highest segregation. The models have been fitted to similar profiles [17] giving good agreement over a range of temperatures and growth rates.

The atomistic picture of segregation is not available but growth and nucleation process is expected to have a strong influence on the segregation. In particular, there is large difference between the SSMBE and GSMBE/CVD which remains to be properly under-

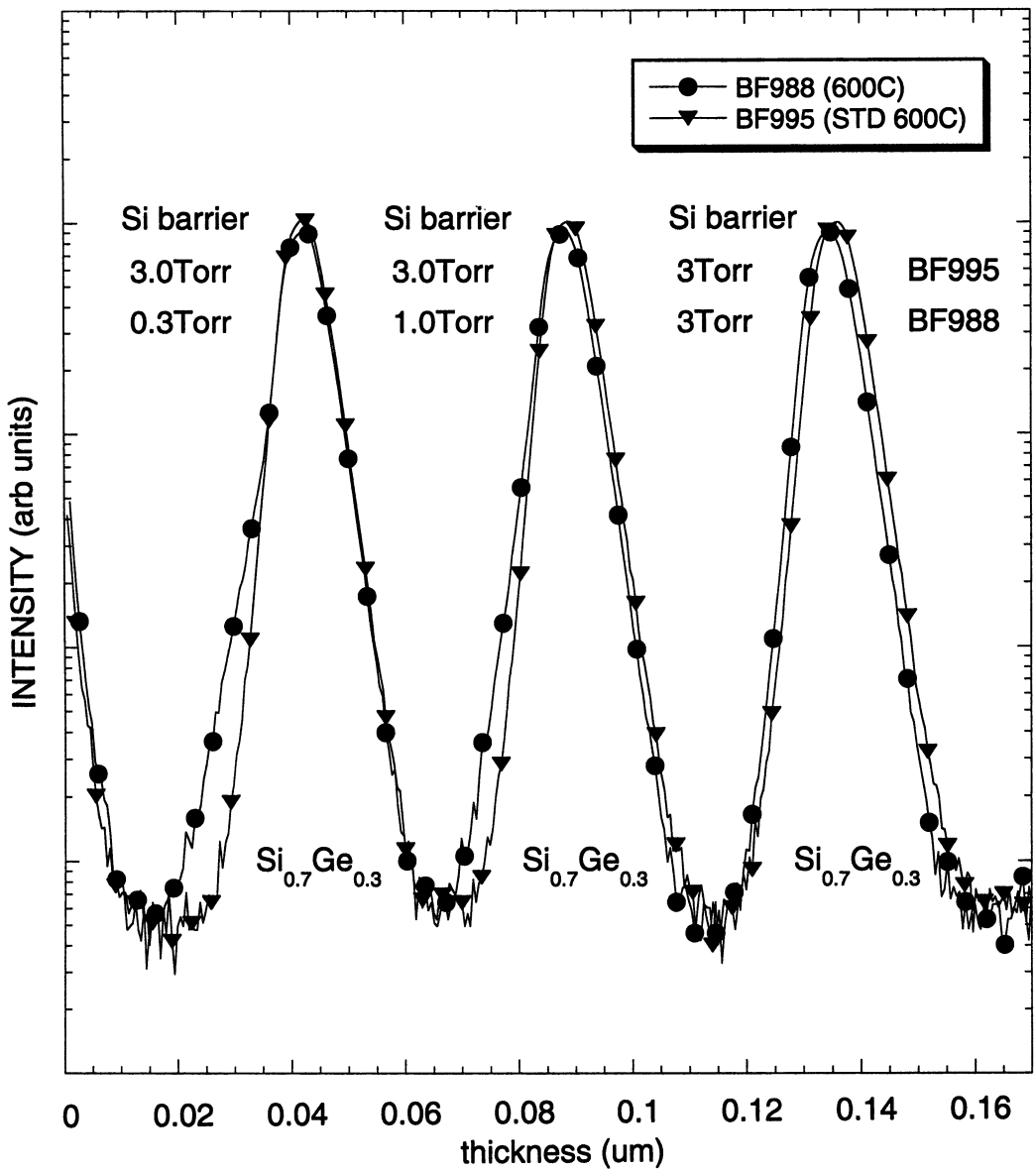


Fig. 3. Comparisons of SIMS composition profiles of Ge under different growth rates (source pressure). The capping layer with the smallest growth rate (0.3 Torr) shows the largest extend of segregation.

stood. The dependence on nucleation is examined as a function of misorientation of the substrate. The decay length obtained showed deterioration when the misorientation angle exceeded 2°. On these samples with large misorientation, the growth is expected to proceed via step flow mode [19] and the presence of steps is expected to modify the nucleation behaviour. However, this experimental finding merely confirms the dependence of segregation on 2D nucleation during growth and an explanation for the observed dependence remains illusive. The result can provide a basis for explaining the difference in segregation of Ge between GSMBE and SSMBE rather than using the presence of hydrogen alone.

In addition to segregation, the concentration profiles of Ge can also be broadened by diffusion process. This is particularly relevant given the high temperature required during oxidation and implant anneal processes. At growth temperatures relevant to GSMBE, diffusion does not play a role in determining the concentration profiles and an anneal at 800 °C for 5 min inside the growth system leaves the Ge concentration profiles measured by SIMS unchanged. However, diffusion is expected to dominate at higher temperatures, in particular where the process is likely to introduce vacancies into the layer.

The arsenic segregation can also be understood using this model. Here the influence of As on the Si growth rate is easier to incorporate [20]. The arsenic atom has valence V, and passivates any surface site against adsorption of hydride precursors in a similar way to hydrogen. This lead to the simple, but approximate, prediction that the growth rate is proportional to $(1-\theta_{As})$ where θ_{As} is arsenic surface coverage [20]. Substituting this into the rate equations, it cancels some of the self-limiting terms and one obtains the simpler rate equation shown below, if hoping into the sub surface site is ignored (this correspond to very slow incorporation of As, as is known experimentally):

$$\frac{dn_s}{dt} = k_+ n_b - \frac{\beta_0 n_s}{a}$$

$$\frac{dn_b}{dt} = -k_+ n_b + \frac{\beta_0 n_s}{a} - \frac{\beta_0 n_b}{a} \quad (4)$$

The solutions reduce to that similar to the dilute regime with two different characteristic decay lengths. The experimental findings using RHEED intensity oscillations [21] and SIMS have clearly shown the presence of two decay lengths with the λ_2 on a scale significant and sometime larger than the thickness of layers employed in devices. In order to achieve sharp doping profiles, the removal of arsenic on the surface can only be achieved by thermal flash off at temperatures in excess of 750 °C.

4. Suppression of threading dislocations in virtual substrate

Compositionally graded virtual substrates have long been adopted to provide the necessary SiGe substrate for heterojunction metal-oxide-semiconductor (HMOS) devices. The problem of threading dislocations is well known [1] and a number of approaches have been adopted to reduce its density including reduction of grading rate. Our previous attempt at introducing a superlattice in the constant composition layer [22] was less successful in achieving this aim due to poor surface morphology produced by growth of very high Ge concentration films. The role threading dislocations play in strain relaxation has long been recognised [23] with the misfit segment actually relieving the strain present in the film. There have been many schemes to improve the strain relaxation processes [24] including parabolic composition grading and incorporation of 'symmetric' superlattice in the grading region. As an alternative approach, layers near critical thickness under compressive strain have been inserted into the linearly graded layer (BF1053) as indicated in the Fig. 4. The aim of these high stress layers is to promote misfit segment of dislocations and thus reducing the total number of dislocations which eventually thread through to the surface. Fig. 5 shows differential interference contrast micrographs of the surfaces of this sample together with that of a reference sample (BF1040) grown at the same grading rate (10% per μm) without the high stress layers. The reduction in threading dislocation density is evident and bunching has virtually disappeared. The effectiveness of strain relaxation is assessed using X-ray diffraction reciprocal space mapping (RSM) measurements. Fig. 6 shows the RSM near the (224) reflection for the two samples. Both samples are near full relaxation but the distribution of intensity due to tilt of the epitaxial film is quite different between the two. The layer (BF1053) with stress inserts appears to have a more symmetric tilting about the substrate with a wider distribution compared with the conventional linearly graded layer (BF1040). The implication of these measurements on electrical properties remains to be characterised.

5. Conclusions

Despite complex reaction kinetics, the advantages offered by epitaxial growth from hydride have led to increasing application of the technique. The basic reactions are well understood with few exceptions and the chemistry involving growth of alloys has also been resolved. The surface segregation process which limits the formation of sharp heterjunctions and doping profiles is well understood in terms of phenomenological

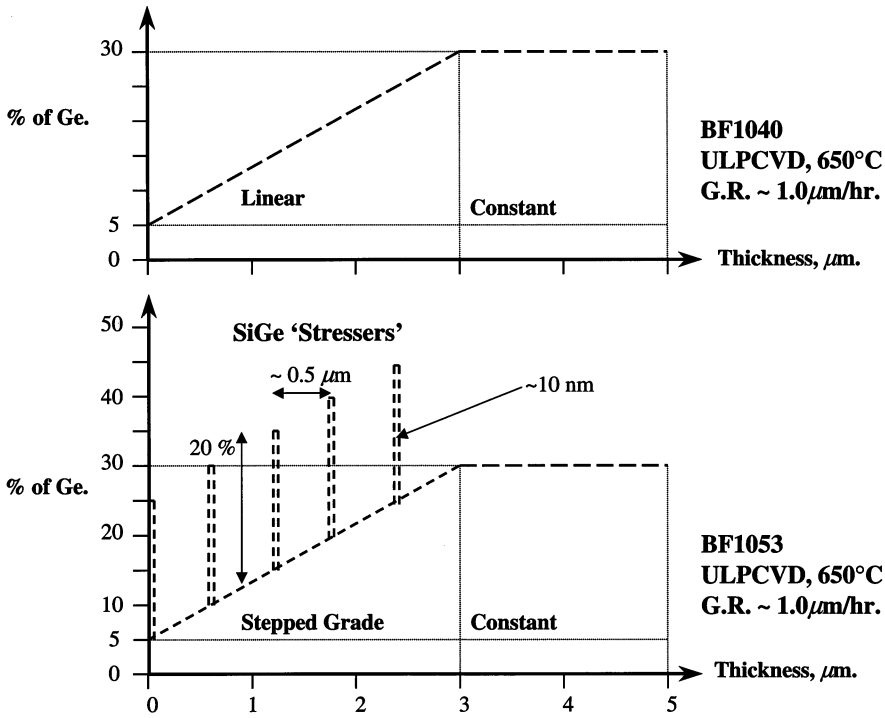


Fig. 4. Schematics of Ge profile in virtual substrates.

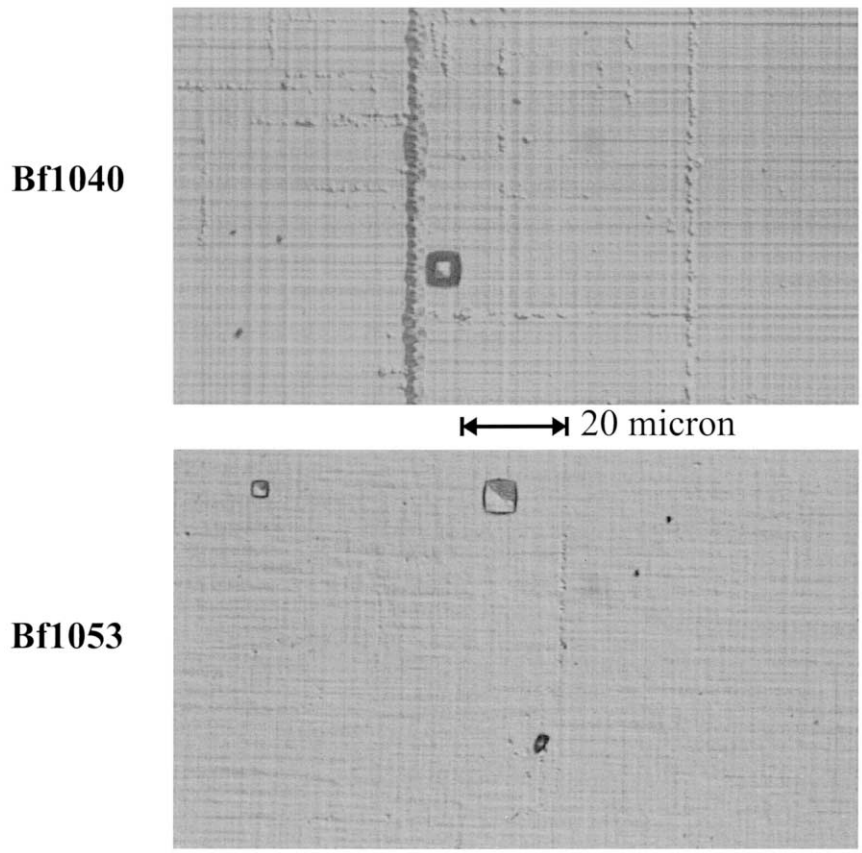


Fig. 5. Differential Interference contrast micrograph of samples with (BF1053) and without (BF1040) stress layers in the graded region.

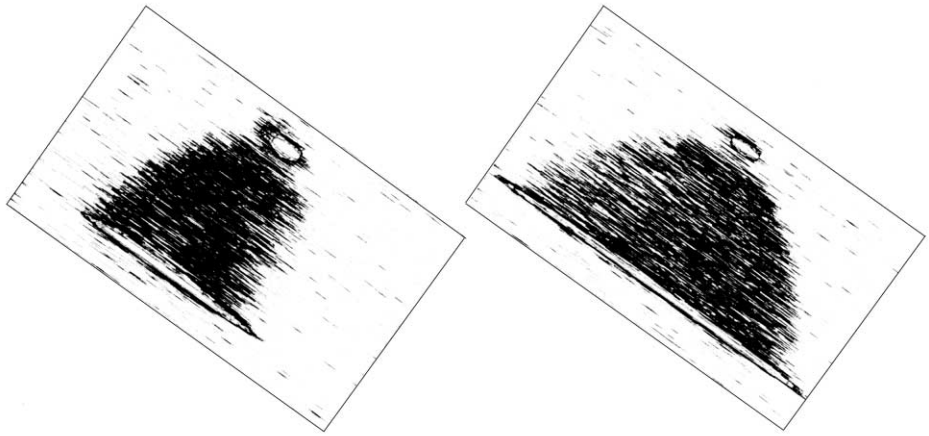


Fig. 6. X-ray diffraction reciprocal space map near the (224) reflection of the samples with (BF1053) and without (BF1040) stress layers in the graded region.

models and efforts are made to understand the atomistic pictures of surface segregation. Along with other approaches such as low temperature Si buffer employed by SSMBE, virtual substrate grown using CVD/GSMBE has developed and provides a basis for modern electronic and optoelectronic applications.

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