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Invited
Low Temperature Epitaxy of Si and SiGe by the Novel Centrifugal LPE Technique

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We have applied rotating crucibles to produce centrifugal forces which are useful for various purposes in liquid phase epitaxy (LPE) and solution growth of semiconductors. In one technique, centrifugal forces serve to transport the solutions in the LPE processes. Layers of Si and SiGe were grown on 100 mm diameter Si wafers and GaAs on 100 mm diameter GaAs wafers. A second technique requires higher rotational frequencies of the crucible. Centrifugal forces influence the local distribution of the solute in the solution. Locally increased solute concentration allows us to prepare multi-crystalline semiconductor layers on dissimilar substrates. In addition, centrifugal forces offer a variety of improvements for crystal growth processes.

1. INTRODUCTION

Liquid phase epitaxy (LPE) has for a long time been used to grow crystalline layers on crystalline materials[1-3]. Since in LPE processes layer growth takes place close to thermodynamical equilibrium, the epitaxial layers have a high structual perfection. Hence, their electronic quality is superior to that of layers grown by other epitaxial techniques such as vapor phase epitaxy (VPE) or molecular beam epitaxy (MBE). However, on the other hand, the equilibrium growth condition makes difficult the growth of layers on amorphous substrates or thin multi-layer growth of different materials. Liquid phase epitaxy, or more generally, solution growth has the advantage that in most cases a purification during the growth process of the layers takes place.

In solution growth, a saturated solution has to be brought in touch with substrates before epitaxial growth starts. After growth, substrates and the solution have to be separated. Many techniques have been developed in order to transport substrates or solutions, i.e. dipping-, tipping boat-, slider boat-techniques, and some others. Dipping- and tipping boat- techniques can be used for growing single layers. These techniques, however, are not suitable for multi-layer growth. Slider boats offers a possibility for multi-layer growth, yet are often combined with scratching of the layers and abrasion caused from the crucible. In order to overcome these difficulties we developed a novel centrifugal technique for crystal growth of semiconductor materials[4-6]. We have applied centrifugal forces, produced by rotating crucibles, for various purposes in semiconductor layer growth from metallic solution.

2. GROWTH TECHNIQUES APPLYING CENTRIFUGAL FORCES

Liquid phase epitaxy requires a growth environment free of contaminants and particles. Contaminants and particles do not only inhibit uniform epitaxial growth of the semiconductor materials but also deteriorate the electronic and optical properties of the layers. Crucible rotation with the help of magnetic bearings provides the opportunity for avoiding contamination caused by lubricants used in mechanical bearings, as well as their abrasion[6,7].

2.1 LPE CENTRIFUGE FOR TRANSPORTING SOLUTIONS

During the LPE process the metal solution, which is saturated with semiconductor materials such as Si, Ge, or GaAs, is transported onto the substrate prior to growth and removed from the substrate after the growth. This solution transport is one of the functions of the centrifugal forces in the LPE procedures. Examples of LPE centrifuges applying centrifugal force for solution transport are described in detail in the literature[4-6]. Combined function of centrifugal and gravitational forces are utilized to achieve the desired solution transport. Several types of crucibles have been designed and used. A cylindrical crucible in which the center of the wafer coincides with its rotational axis is suited for single-layer growth on large diameter (e.g. 100 mm) wafers. For multi-layer growth a crucible in which several substrates are arranged excentrically around a rotational axis proved to be suitable. In all cases there are no moving crucible parts necessary for layer growth. Abrasion from the crucible and scratching of the grown layers thus avoided. Rapid solution transport produces brief contact between solution and substrates. It is, therefore, possible to grow extremely thin layers. The solution may be completely spun away from the substrate.

2.2 CRYSTAL GROWTH FROM THE SOLUTION UNDER CENTRIFUGAL FORCES

A second application of centrifugal forces for crystal growth from solution consists in changes in solute concentration in the solution[14]. Solute concentration changes because of the difference in molar volumes between solute and solvent. Traditionally, temperature differences serve to create concentration gradients in the solution. By the application of centrifugal forces it is possible to create isothermally concentration gradients of the solute in solution. High super-saturation of the solutions can also be obtained using this technique, yet without cooling the system. High rotational speed of the crucible is required to create sufficiently large centrifugal forces.

New features are nucleation and crystal growth under the effects of centrifugal forces. For example, it is difficult to grow layers of rough surface by conventional LPE technique because of the high surface tension of the metallic solution. Using the centrifugal forces the solution can be driven into pores of the substrates. Nucleation and growth then start in these pores.

3. FEATURES OF THE EPITAXIAL LAYERS GROWTH BY CENTRIFUGAL TECHNIQUES

3.1 SOLUTION TRANSPORT BY CENTRIFUGAL FORCES

3.1.1 MULTI-LAYERS

Multi-layers of pnpn Si have been grown in LPE centrifuges[4,5]. An example is shown in Fig. 1. A multi-layer of 15 p-type and 15 n-type layers was grown alternately from Ga- and As-doped indium solutions in temperature intervals of 836 - 827 and 836 - 820 °C, respectively. The p-type layers have a thickness of about 0.6 μm; the n-type layers are 1.2 μm thick. Dopant concentration in both layers are about 1×10^{18} cm^{-3}. The carrier concentration of LPE layers is adjusted by the amount of dopant materials added to the solution. The carrier concentration of Ga-doped, p-type Si varied between 8×10^{15} cm^{-3} when grown from pure In solution and 2×10^{19} cm^{-3} when grown from pure Ga solution. We obtain As-doped, n-type Si with carrier concentrations between 3×10^{17} and 3×10^{19} cm^{-3}.

GaAs multi-layers in which Ge-doped and undoped layers are stacked alternating were also grown[9].

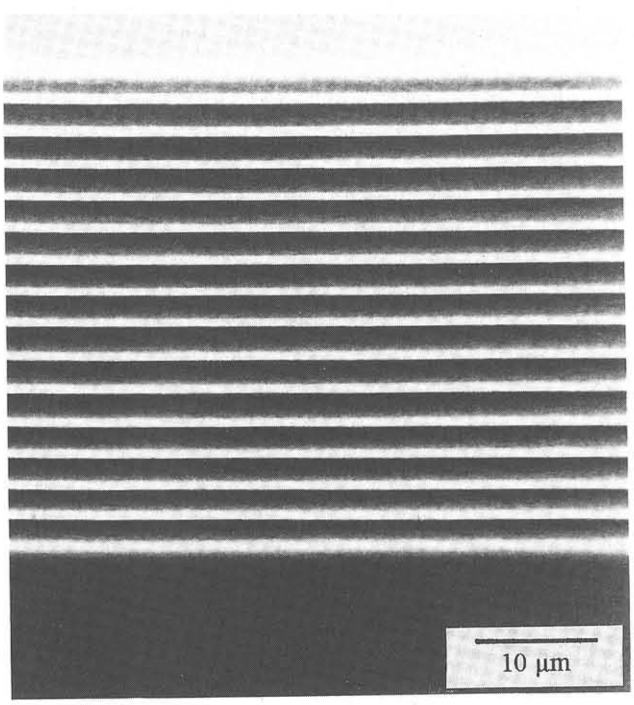

Fig. 1 Silicon multi-layer grown from In:Ga- and In:As-solutions to produce an alternating p-n structure.

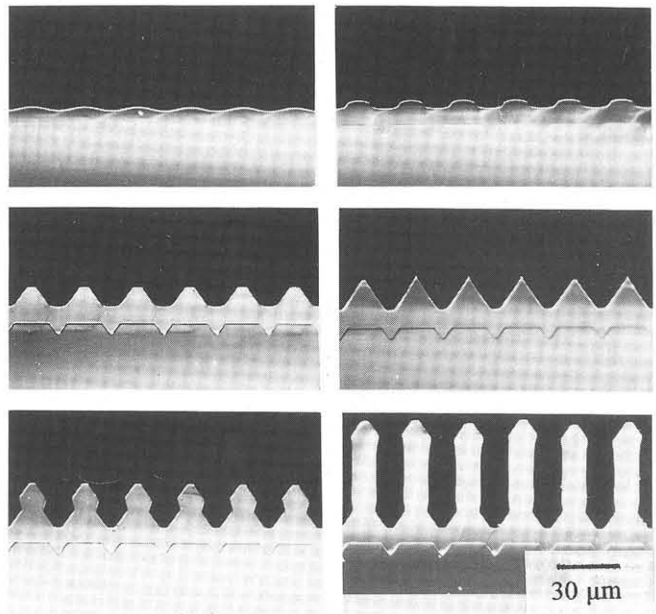

Fig. 2 Roof and vertical parallel lamellar shaped Si LPE layers grown on mono-crystalline (100) substrates. The substrate surfaces have V-shaped grooves extending along <110> direction

3.1.2 LPE ON TEXTURED OR MASKED SURFACES

The {111} face is the most stable crystallographic face of Si. Its stability becomes apparent when LPE layers are grown from the solvents In, Ga, or Bi. Faces being {111} oriented begin to develop during the LPE process whenever {111} planes are tangential to the crystal's growth face. We have applied these characteristics for growing layers with various surface shapes[9,10]. A roof-shaped structure as shown in Fig. 2 forms on a Si substrate, whose surface is patterned with shallow V-shape grooves extending along <110> directions. Patterning is done by standard photolithography and wet etching. These layer structures were grown from In solution at 920 °C. Different shapes of the layer surfaces, varying from vertical parallel and lamellae-shaped structures with a roof shaped top to a shallow wave like surface can be formed by decreasing the cooling rate.

Pyramid-shaped surfaces are obtained by employing a (100) oriented substrate which has a thermally-grown oxide mask with square shaped windows.

3.1.3 SOI STRUCTURES

When silicon LPE is performed using a mono-crystalline (111) Si substrate with line shaped openings through a thin thermal oxide, laterally grown defect-free SOI (semiconductor on insulator) layers can be produced[11,13]. As shown in Fig. 3, silicon layer growth starts from the line shaped seed regions. There steps exist which result from a small off-orientation of the substrate. When the top of the epitaxial layer exceeds a critical level, crystal growth starts laterally over the oxide. The aspect ratio, which is determined by the maximum

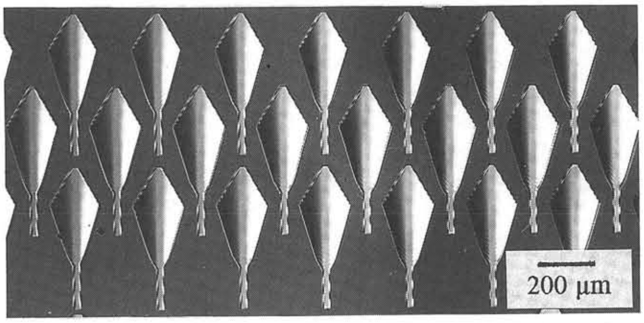

Fig. 3 Examples of defect-free SOI lamellae obtained by LPE. Substrate off-orientation $\delta = 0.3$ °.

distance of the laterally over-grown region divided by the layer thickness, reaches 65.

Epitaxial layers of Ge and its solid solution with Si have been grown using this particular structure on Si substrates. Dislocations originating from the lattice constant miss-match between epitaxial layer and substrate, can be confined to the seed regions. Dislocation-free Ge layers, however, form on the thermally grown Si oxides utilizing this epitaxial lateral over growth (ELO).

3.1.4 LPE ON 100 mm DIAMETER WAFERS

Silicon epitaxy has been performed on 100 mm diameter mono-crystalline Si wafers[6]. The thickness uniformity of the layer within the central wafer area of 90 mm diameter is better than $\pm$4.9 %. Silicon/ Germanium on mono-crystalline Si wafer, Si on multi-crystalline Si wafer[12], and GaAs on mono-crystalline LEC grown GaAs wafer[8] have also been grown on 100 mm diameter wafers.

3.2 UTILIZING THE EFFECTS AT HIGH ROTATIONAL SPEED OF THE CRUCIBLE

3.2.1 MULTI-CRYSTALLINE FILM GROWTH ON POROUS GLASS

Figure 4 shows a poly-crystalline Ge layer grown on a porous silica glass[14]. Germanium crystals were grown

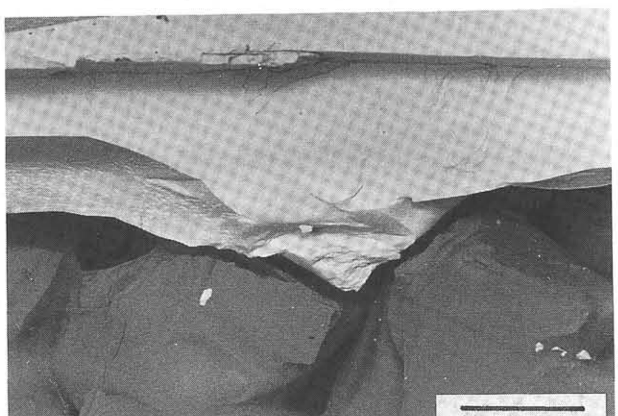

Fig. 4 Poly-crystalline Ge layer grown directly on sintered porous silica glass.

from In solution in a temperature range of 840 - 600 °C. During growth the crucible was rotated at a rotational speed of 2000 rpm which creates centrifugal forces as high as 100 g_n (g_n denotes the standard acceleration of free fall: 9.807 ms^{-2}). Centrifugal forces drive the solution into pores of the sintered silica glass. Nucleation and growth start in these pores and crystals grow outwards from these pores. The grown layers adhere firmly to the substrates.

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