Effect of Growth Direction on Twin Formation in GaAs Crystals Grown by the Vertical Gradient Freeze Method

A.N. Gulluoglu[1], **C.T. Tsai**[2]

Abstract: Twins in growing crystals are due to excessive thermal stresses induced by the temperature gradients developed during the growth process. Twinning is an important defect in advanced semiconductor crystals such as GaAS and InP. The objective of this study is to develop a computational model to predict the twin formation in the Gallium Arsenide (GaAs) crystals grown by the vertical gradient freeze method (VGF). A quantitative quasi-steady state thermal stress model is developed here for predicting the twinning formation in GaAs grown by VGF. The thermoelastic stresses in VGF grown crystal are calculated from a two-dimensional finite element analysis. Deformation twins form as a result of the high shear stresses acting on the twinning plane and in twinning direction. In the study, the resolved shear stress (RSS) distributions in the twin systems for different growth directions have been calculated. This investigation is expected to further the understanding of twinning formation during crystal growth for different growth direction.

keyword: Twinning, crystal growth, the Gallium Arsenide, Vertical Gradient Freeze method.

1 Introduction

There has been an increasing demand for high quality GaAs and InP single crystals for high-speed electronic and optical devices. In response to these demands, new techniques have been developed for investigation of growth parameters for growing low defect crystals. The vertical gradient freeze (VGF) method has been developed (Gault, Monberg, and Clemans, 1986), which is a novel process to grow III-V semiconductor crystals with large diameter and low defect. Twins are generated in GaAs due to excessive thermal stresses induced by thermal gradient during growth. The VGF technique can achieve a low thermal gradient via an empirically optimized combination of insulation, heat shields and the spatial distribution of heat input. It is well known that the crystal defects in these materials adversely affect the lifetime and performance of these devices (Jordan, Von Neida, and Caruso, 1986). For example Brantley and Harrison (1973) have observed that the degradation rate in diffused electroluminescent diodes increased by an order of magnitude.

It is known that deformation twins form as a result of the shear stress acting on the twinning plane and in the twinning direction. The theoretical shear stresses necessary for a homogenous nucleation of a deformation twin in a crystal lie between 1/30 to 1/500 μ of the theoretical elastic limits (Friedel,1964). This is a strong evidence for the belief that twins are nucleated heterogeneously in the regions of high stress concentration in the crystal. Formation of deformation twins depends strongly on the temperature gradient present during crystal growth, non-skoichiometry of the melt, and facet growth. Deformation twins are formed when the resolved shear stress (RSS) in the twinning system of the crystal exceeds the critical resolved shear stress (CRSS) for twinning formation. Even though the experimental data for CRSS of GaAs are not available at present, the development of a numerical model for predicting twins formation is valuable by assuming a CRSS to provide comparative study of twins formation for various growth conditions and crystals. This comparative study will provide valuable information to improve the understanding of the twin formation in GaAs crystals grown from the melt. Furthermore, it can be employed for optimizing the growth configurations and parameters for growing GaAs crystals with little twin formation. If one can obtain the CRSS from the experimental measurements, the data can be directly applied to the developed model and more accurate results can be obtained. In the following section, the basic simulation procedure for studying the twin growth is summarized. Results of numerical simulations are presented and analyzed in Sec. 3. Finally, the last section presents a discussion of the numerical results.

2 Simulation model of twinning formation

In the crystal growth processing which is shown in Fig. 1, a cylindrical ingot with a near planar solid-liquid interface (T_m) is solidified from the melt at rate p by the vertical gradient freeze method developed (Gault, Monberg, and Clemans, 1986). The temperature fields, which are used to model the residual stress state and twin formation in the crystals, are calculated from a quasi-steady-state heat transfer model (Jordan and Monberg, 1993). In the model, the growing crystal ingot is assumed to be an axisymmetrical solid (Fig. 1). If u and w are displacement components in the r and z directions, respectively, then the strain components in the cylindrical coordinates are

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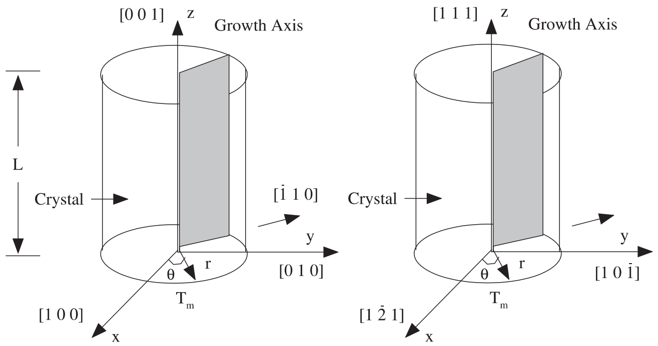


(a) (b)

Figure 1 : Coordinate system of the crystal pulling (a) the [0 0 1] and (b) the [1 1 1] direction during crystal growth, where T$_m$ is the melting point along the solid-melt interface of the crystal.

Table 1 : The 12 permissible twinning systems for GaAs.

Twinning System	Twinning Plane	Twinning Direction
1	1 1 1	-1 -1 2
2	1 1 1	1 -2 1
3	1 1 1	2 -1 -1
4	1 -1 -1	2 1 1
5	1 -1 -1	1 2 -1
6	1 -1 -1	-1 1 -2
7	-1 1 -1	1 2 1
8	-1 1 -1	-1 1 2
9	-1 1 -1	-2 -1 1
10	-1 -1 1	1 -2 -1
11	-1 -1 1	2 -1 1
12	-1 -1 1	1 1 2

$$\varepsilon_{rr} = \frac{\partial u}{\partial r}, \ \varepsilon_{\theta\theta} = \frac{u}{r}, \ \varepsilon_{zz} = \frac{\partial w}{\partial z}, \ \varepsilon_{rz} = \frac{1}{2}\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right). \qquad (1)$$

By assuming GaAs crystal as an elastically isotropic material, the stress-strain relations are

$$\left\{\begin{array}{c}\sigma_{rr}\\ \sigma_{\theta\theta}\\ \sigma_{zz}\\ \sigma_{rz}\end{array}\right\} = \frac{E}{(1+\nu)(1-2\nu)} \times$$

$$\left[\begin{array}{cccc}(1-\nu) & \nu & \nu & 0\\ \nu & -\nu & \nu & 0\\ \nu & \nu & (1-\nu) & 0\\ 0 & 0 & 0 & \frac{1-2\nu}{\nu}\end{array}\right]\left\{\begin{array}{c}\varepsilon_{rr}-\alpha\Delta T\\ \varepsilon_{\theta\theta}-\alpha\Delta T\\ \varepsilon_{zz}-\alpha\Delta T\\ \varepsilon_{rz}\end{array}\right\}. \qquad (2)$$

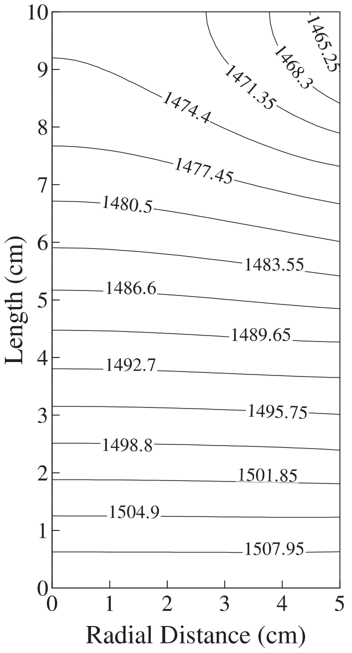


Figure 2 : Temperature distribution in the crystal grown by VGF.

where, E, ν and α are Young's modulus, Poisson's ratio, and thermal expansion coefficient of GaAs, ΔT is the temperature change, subscripts rr, $\theta\theta$ and zz refer to the r, θ and z coordinate system of Fig. 1. Based on Eq. 1-2 and the principle of virtual work, a finite element equation for the thermal-elastic problem of quasi-steady-state crystal growth in terms of displacement fields is given by Zienkiewicz (1978) as

$$[K_s(T)]\{U\} = \{F_T\} + \{F_\sigma\} + \{F_b\} = \{F\} \qquad (3)$$

where $[K_s(T)]$ is the stiffness matrix, which is a function of temperature; U represents the nodal displacements u and w; and the terms on the right hand side are thermal loading (F_T), surface tractions (F_σ) and body forces (F_b), respectively.

The thermal stress calculations are performed in the cylindrical coordinate system in which the z-axis is assigned to be a growth axis in these simulations, either [0 01] or [1 11] as shown in Fig. 2. In the simulations, x//[1 0 0], y//[0 1 0] and z//[0 0 1] are chosen in the case of crystal growth direction of [0 0 1], and if the growth direction is [1 1 1], x//[1 -2 1], y//[1 0 -1] and z//[1 1 1] are selected. The cylindrical stress components σ_{rr}, $\sigma_{\theta\theta}$, σ_{zz} and σ_{rz}. are transformed into the Cartesian coordinate system by use of the stress transformation tensor, $\sigma_{ij} = \sigma_{kl} l_{ik} l_{jl}$, where l_{ik} and l_{jl} are direction cosines, ($i, j, k, l = 1, 2, 3$), σ_{ij} and σ_{kl} are stress tensors in Cartesian and cylindrical coordinate system, respectively.

The major mechanism for the introduction of twins during crystal growth is excessive thermal stress. GaAs crystals have crystal structure of diamond. The twining plane in the diamond cubic case is $\{111\}$ and twinning directions are <112>. There are a total of 12 twin systems that can be considered

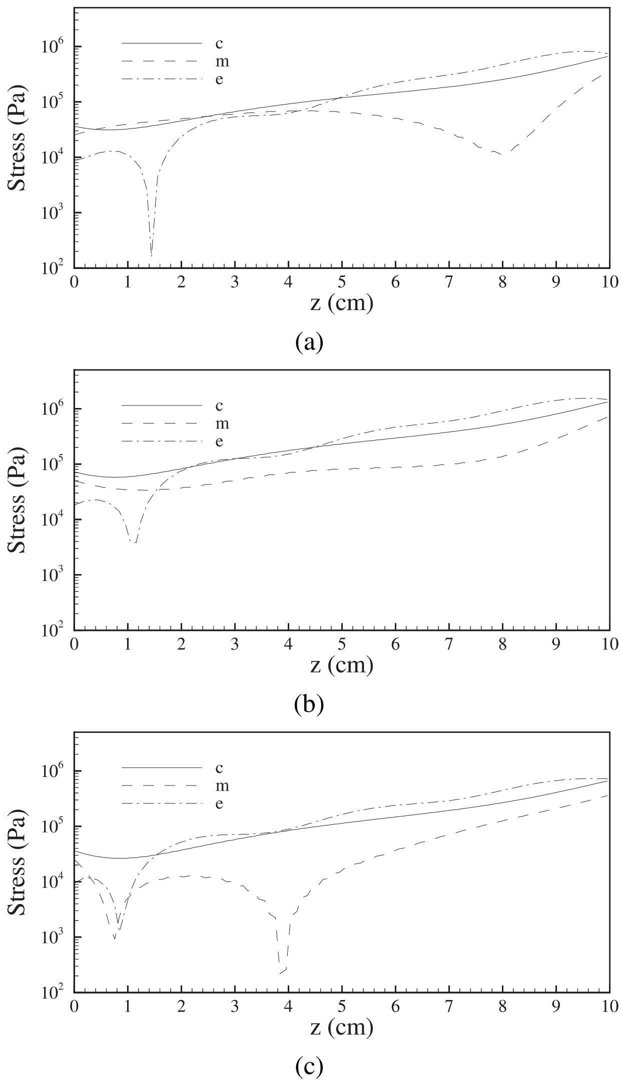


Figure 3 : Resolved shear stresses on (1 -1 0) plane along the [0 0 1] growth direction near the center, the middle, and the edge, of the wafer for (a) (-1 -1 1)[1 1 2], (b) (-1 1 -1)[-1 1 2] and (c) (-1 1 -1)[-2 -1 1] twin systems.

in the present crystal system (Yasutake, Shimizu, Umeno and Kawabe, 1987). Those 12 permissible twin systems are listed in Tab. 1. Formation of twins depends on the magnitude and directions of the stresses on twinning systems. A necessary condition for twinning is that the shear stress resolved on the twinning plane and in the twinning direction shall reach the critical resolved shear stress (CRSS) which is characteristic of the crystal. A local coordinate system (x', y', z') is defined for calculation of RSS in each twinning system in which twinning direction is along x', y' is normal to the twin plane, and z' is parallel to cross product of x' and y' vectors. The global stress tensor in Cartesian coordinate system is transformed into the local coordinate system of the twin by use of

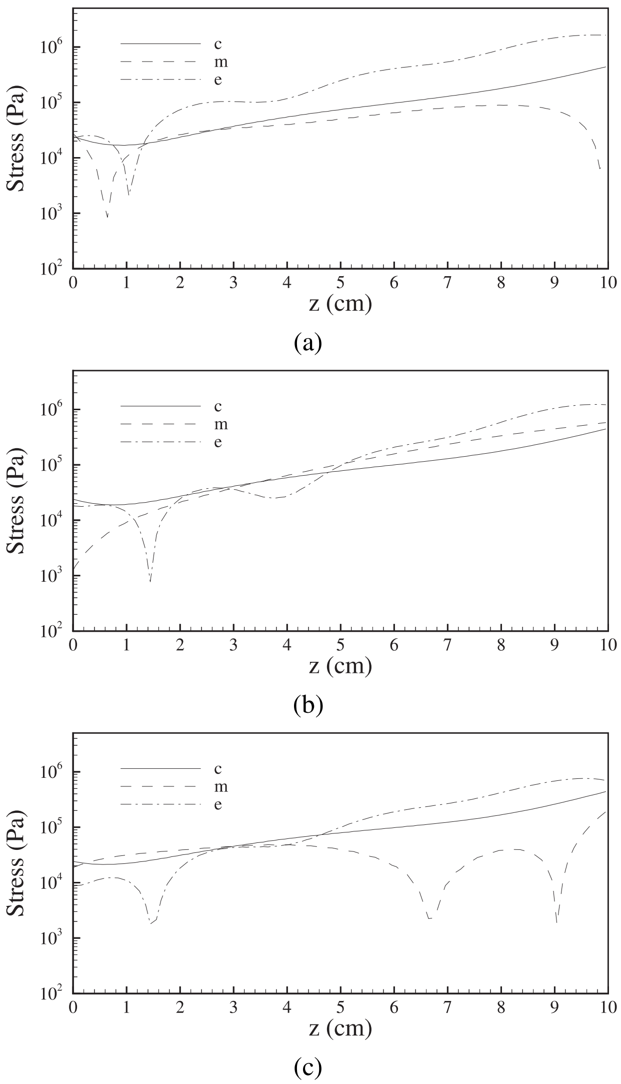


Figure 4 : Resolved shear stresses on the plane between (1 0 -1) and (1 -2 1) (in Fig. 1b) along the [1 1 1] growth direction near center, the middle, and the edge of the wafer for (a) (-1 -1 1)[1 1 2], (b) (-1 1 -1)[-1 1 2] and (c) (-1 1 -1)[-2 -1 1] twin systems.

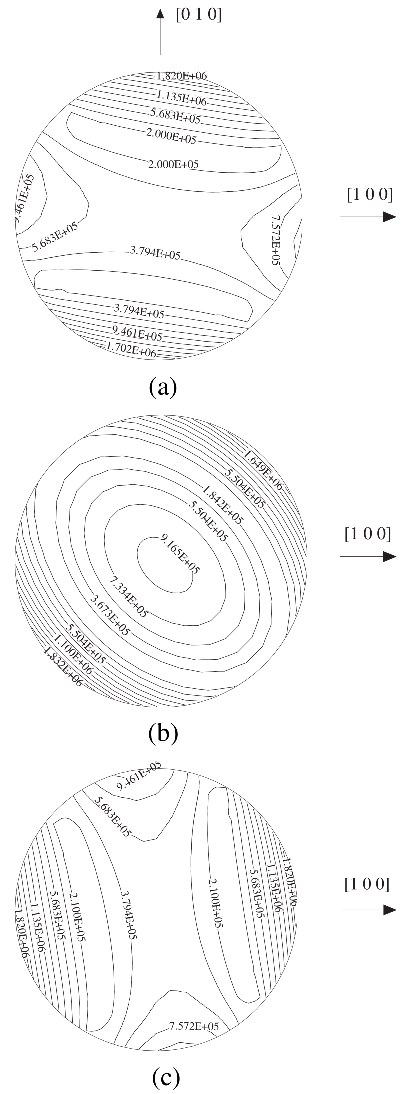
the stress transformation tensor, $\sigma_{i'j'} = \sigma_{kl} l_{i'k} l_{j'l}$ where $\sigma_{i'j'}$ and σ_{kl} are stress tensor in local and global coordinate systems, respectively. The RSS acting on the 12 twinning systems are then calculated using this model.

3 Results and discussions

The numerical result of GaAs ingot grown by a vertical gradient freeze method is presented as an example for investigation of twin formation in the crystal using the crystallographic model. The temperature profiles and the solid-meld interface (melting point of GaAs, 1511 K) shape for the VGF growth GaAs crystal after about 25 hours of growth (10 *cm* long crystal) are shown in Fig. 2. The imposed temperature gradient on the periphery of the GaAs boules grown by VGF was -5 K/cm. The radius of the ingot is 5 *cm*, and the length is about 10 *cm*. The growth rate is 1.16×10^{-4} cm/s.

The major factors influencing the deformation twin formation are the temperature profile during the growth of crystal and resulting thermoelastic stresses. Twinning depends on the magnitude and direction of resolved shear stress on the twin systems. The effect of crystal growth direction on defect concentration has been investigated for the [0 0 1] and [1 1 1] pulling directions using the temperature distribution obtained by solving the partial differential equation for heat conduction with a cylindrical symmetry and moving source of heat on the surface of boules. The effect of temperature gradient along the growth direction on twin formation in each twinning system has been studied, and the resolved shear stresses on (1 -1 0) plane along the growth direction of [0 0 1] near the center (r=0.1 *cm*), the middle (r=2.5 *cm*), and the edge (r=4.8 *cm*), of the wafer for (-1 -1 1)[1 1 2], (-1 1 -1)[-1 1 2] and (-1 1 -1)[-2 -1 1] twin systems with larger RSS is shown in Fig. 3a-3c. Fig. 4 shows the resolved shear stresses on the plane between (1 0 -1) and (1 -2 1) (in Fig. 1b along the [1 1 1] growth direction near the center, the middle, and the edge of the wafer for (a) (-1 -1 1)[1 1 2], (b) (-1 1 -1)[-1 1 2] and (c) (-1 1 -1)[-2 -1 1] twin systems which have larger RSS. It can be seen from Fig. 3 that resolved shear stresses near the edge and center of the wafer are much greater than that near the midway of the wafer along the growth direction of [0 0 1]. On the other hand, Fig. 4 shows that resolved shear stresses near the edge of the wafer are much greater for the crystal growth direction of [0 0 1].

Calculated resolved shear stresses in the 1 1 1, <1 1 -2> twin systems for GaAs crystal grown for either of two principal growth directions, [0 0 1] and [1 1 1] by VGF (Fig. 3-4) show that the maximum shear stresses are always located near the top of the crystal. Therefore, contour maps for resolved shear stresses on the (001) GaAs wafer near the top of the crystal are studied for each twinning system along the growth direction of [0 0 1] and shown in Fig. 5 for twin systems (a) (-1 -1 1)[1 1 2], (b) (-1 1 -1)[-1 1 2] and (c) (-1 1 -1)[-2 -1 1]. Fig. 6 shows contour lines of resolved shear stresses on the (1 1 1) plane for (a) (-1 -1 1)[1 1 2], (b) (-1 1 -1)[-1 1 2] and (c) (-1 1 -1)[-2 -1 1] twin systems in the GaAs wafer for crystal grown along [1 1 1] pulling direction. Resolved shear stress contour lines for the 12 twinning systems show that there are only two different distribution patterns. One shows the elliptical contour lines through the wafer with high resolved shear stress at the center of wafer, after decreasing at the midway, the RSS reaches its largest value along the short axis of ellipse near the edge of the wafer. Another shows like four-fold symmetric contour lines, with low RSS at the center and along the symmetry lines. For each twinning plane, there is always one twinning direction having an elliptical contour line stress pattern and two twinning directions having a four-fold symmetric contour line pattern. For the GaAs crystal grown by VGF process along the [0 0 1] pulling direction, the resolved shear stress attains its maximum value of 1.8×106 *Pa*, at the edges of the wafer. The twinning systems having maximum stress values are the twinning systems having like four-fold symmetric stress distribution pattern. Fig. 6 illustrates that largest resolved shear stresses, which are about 1.9×106 *Pa*, in the GaAs wafer grown along [1 1 1] direction and appears normal to the direction lying along the four directions at 45^o to the [1 0 -1] and [1 -2 1] directions for the area very edge of the wafer. If the CRSS for GaAs is greater than the largest calculated resolved stresses, no twinning will occur. Otherwise, twinning could occur in any twinning system as long as the RSS in this twinning system are greater than the CRSS. Since the CRSS for the GaAs is not available at present, we will present the



(a)

(b)

(c)

Figure 5 : Resolved shear stresses distribution in the (001) GaAs wafer near the top of the boule for (a) (-1 -1 1)[1 1 2], (b) (-1 1 -1)[-1 1 2] and (c) (-1 1 -1)[-2 -1 1] twin systems.

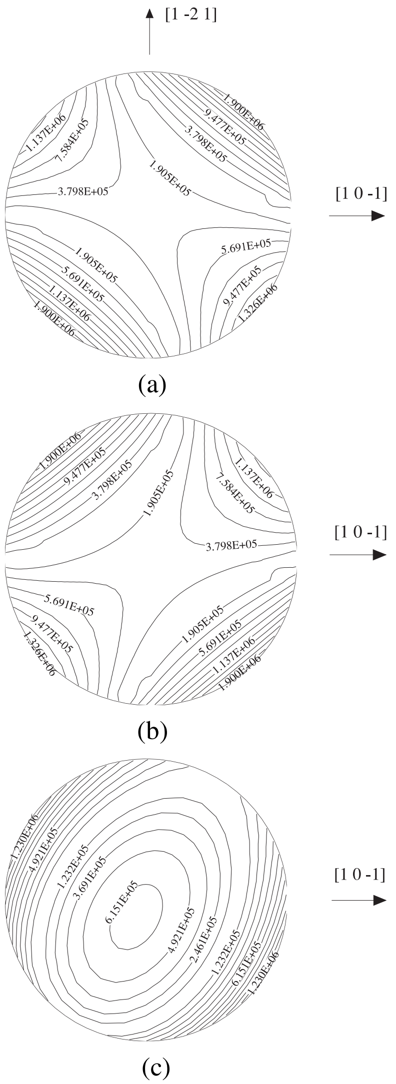


Figure 6 : Resolved shear stresses distribution in the (1 1 1) GaAs wafer near the top of the boule for (a) (-1 -1 1)[1 1 2], (b) (-1 1 -1)[-1 1 2] and (c) (-1 1 -1)[-2 -1 1] twin systems.

contour plot of the RSS, which shows the distribution of possible formation of deformation twins in the crystal. Therefore, results show that a crystal grown in [111] direction will have more deformation twins than that grown in [001] orientation.

4 Conclusion

A quantitative quasi-steady state thermal stress model is developed for predicting the possible deformation twinning in GaAs crystals grown by the VGF. The model indicates a characteristic like four fold symmetric high resolved shear stress pattern in some twin systems with higher possibility of twin formation on (001) and (111) wafers. The calculated resolved shear stresses in twin systems in the grown crystal show a strong dependence on the temperature profile and growth direction. If the CRSS for GaAs is greater than the RSS, no thermal stress generated twin will occur. Otherwise, a twin could be generated in any twinning system. Numerical models of RSS such as the one presented here, may allow using iterative design for growth of GaAs crystals with a few deformation twins through the control of furnace temperature profile and pulling direction during crystal growth.

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