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CONTROL OF SUPERLATTICE MORPHOLOGY IN $GaAs_{1-x}P_x$ CASCADE CELLS

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INTRODUCTION

$GaAs_{1-x}P_x$ superlattices are being incorporated into cascade solar cell structures in order to reduce the dislocation density in the top cells and thus reduce recombination loss and increase output voltage.[1] For a superlattice to effectively block the propagation of dislocations, its average composition must be equal to that of the layer beneath it[2] (from efficiency considerations for a cascade cell, the average composition should be about $GaAs_{.7}P_{.3}$).

When superlattices of this approximate composition were grown on GaAs by MOCVD, severe distortion of the crystal layers was observed. The essential features of this distortion are nonplanar morphology and accelerated etching in regions containing excess phosphorus and clusters of dislocations. Similar observations have been made with superlattices grown with two other MOCVD systems[3], indicating that the problem is of fundamental technological significance, not just an artifact of one particular growth system. This paper describes the nature of the distortion effect and presents several strategies for preventing its occurrence.

EXPERIMENTAL

The multilayer specimens were grown by standard MOCVD techniques, using $Ga(CH_3)_3$, AsH_3 and PH_3 as the primary sources. The substrates were GaAs wafers misoriented 2° from the (100) plane. Computer control was used to set the gas flows through mass flow controllers and rapidly switch them for growth of a superlattice. The composition of the superlatttice was governed by the duration of and PH_3/AsH_3 ratio in the alternating gas pulses. The multilayers were examined by Nomarski optical, scanning electron microscope, electron microprobe, and transmission microscope techniques.

RESULTS

The morphology of the cleaved and etched specimens exhibited a wide range of appearance, varying from flat, parallel, nearly perfect superlattice bands to samples containing extremely distorted layers. Figure 1 shows examples of a flat and a distorted superlattice. The distortion is seen to consist of two components. One is a warping of the sublayers, yielding traces of progressively nonplanar vapor-solid interfaces. The other is a roughly sinusoidal deviation in and out of the cleavage plane, caused by nonuniform action of the etchant over the originally planar cleaved surface. The sites of maximum etching are also the centers of dense dislocation clusters, as revealed by transmission electron microscopy (figure 2), which also provided the information that these regions contain an excess of phosphorus.

If no other layers are grown above the superlattice, its top surface can be observed microscopically, and if distortion is present a cellular texture is seen on this surface. The average period of the cells corresponds to the spacing of the etch streaks traversing the superlattice.

Numerous variations in the growth procedure were investigated in order to learn how to eliminate the distortions. The largest effect was achieved by minimizing the interlayer misfit, Δf, i.e. the interlayer compositional difference, Δx, while keeping the average value of x constant. For example, the $GaAs_{.75}P_{.25}/GaAs_{.65}P_{.35}$ ($\Delta x = .10$) superlattice shown in figure 1a is planar, whereas the $GaAs_{.8}P_{.2}/GaAs_{.6}P_{.4}$ ($\Delta x = .20$) superlattice of figure 1b shows considerable distortion.

Another key factor determining the amount of distortion was the rate of growth of the superlattice. It is usually true that slow growth favors the development of better crystallinity, but in the present situation that is not the case. In an experiment where the run conditions were such as to cause a wide variation in growth rate across a 2-cm wafer, it was noticed that the superlattice quality was very much better in the faster-growing central part of the wafer. In subsequent experiments where the growth rate was uniform, increasing the growth rate by factors of two or more produced distortion-free superlattices.

It has also been found that lowering the growth temperature reduces the tendency toward layer distortion, and increasing the total pressure of Group V hydrides in the source gas increases this tendency. Although not as dramatic as the affects of the factors described above, a significant difference in distortion could be seen between layers grown at 715 °C and at 800 °C and between layers where the total hydride pressure (ratio kept constant) differed by a factor of three.

An important requirement in the prescription of Matthews and Blakeslee[2] for a superlattice to block dislocation propagation is that a compositionally graded layer be grown between the substrate and the superlattice. It has been found that such a layer is also beneficial in reducing the tendency toward distortion. The shallower the concentration gradient, the less severe the distortion. However, this is perhaps the least effective remedy of all those discovered. Flat undistorted layers can probably be grown without any graded layer if the other beneficial factors are sufficiently optimized, although they might not act as dislocation filters.

POSSIBLE MECHANISMS

The distortion of $GaAs_{1-x}P_x$ superlattices has been extensively characterized, and several crystal growth procedures have been developed for reducing or eliminating it, but the basic cause of the inhomogeneity leading to the distortion has not been established. Several possible mechanisms for the distortion have been considered, but so far no single one is in keeping with all the experimental evidence. The main points of several of these hypotheses are addressed in the following.

Diffusion-Induced Disorder

Interdiffusion of $Al_xGa_{1-x}As$ and $GaAs_{1-x}P_x$ superlattice layers has been thoroughly investigated in recent years.[4] In this effect, which is promoted by high anneal temperatures and high concentrations of Zn or other dopants, the interlayer barriers wash out and the material becomes a uniform ternary alloy. In the present case the barriers are not eliminated; rather the whole superlattice is disturbed or destroyed at isolated locations, and the distortion is independent of whether the layers are Zn-doped or undoped. Therefore a mechanism of diffusional disorder does not appear to be operative here.

Elastic Stress

The large improvement in morphology brought about by reducing the interlayer misfit (or its attendant compositional difference) must somehow be taken into account in any tenable explanation of the phenomenon. Yet it is difficult to envision how unrelieved elastic stress per se could produce the observed phenomena. It seems more likely that the misfit stress acts in some as yet unknown manner to magnify the effects due to the operation of some other mechanism.

Constitutional Supercooling

The cellular texture and streaked etch patterns are strongly reminiscent of nonuniform segregation effects associated with constitutional supercooling. By pre-pyrolyzing the PH_3, it was possibly to strongly decrease the phosphorus concentration gradient in the growth system, which should decrease the likelihood of constitutional supercooling. However, this experiment did not improve the morphology at all, and anyhow the fact that increasing the growth rate decreases the distortion is inconsistent with the hypothesis of constitutional supercooling.

Impurity Segregation

Bauser and Rozgonyi[5] have studied heterogeneous impurity incorporation in Czochralski-grown Si and Ge crystals and liquid phase epitaxial GaAs. They observed etching striae in crystals which are similar to the etch figures of the present work. They have developed a generally applicable model of terrace growth which can explain the occurrence and properties of their striations. Their model is being studied because of the possibility that it can be extended to explain the distortion of $GaAs_{1-x}P_x$ superlattices and the etch striations which occur in them. Such a model would predict the observed dependence on growth rate, since rapid growth would cause fewer impurities to accumulate at the growth steps.

Other

Several papers have been published recently attributing observations of inhomogeneous deposition of ternary III-V semiconductor layers to the phenomenon of spinodal decomposition.[6], and nonuniform growth of Si/Ge superlattices has been associated with three-dimensional nucleation.[7]. Both of these mechanisms are currently under investigation as possible causes of the morphological instabilities observed in the present work.

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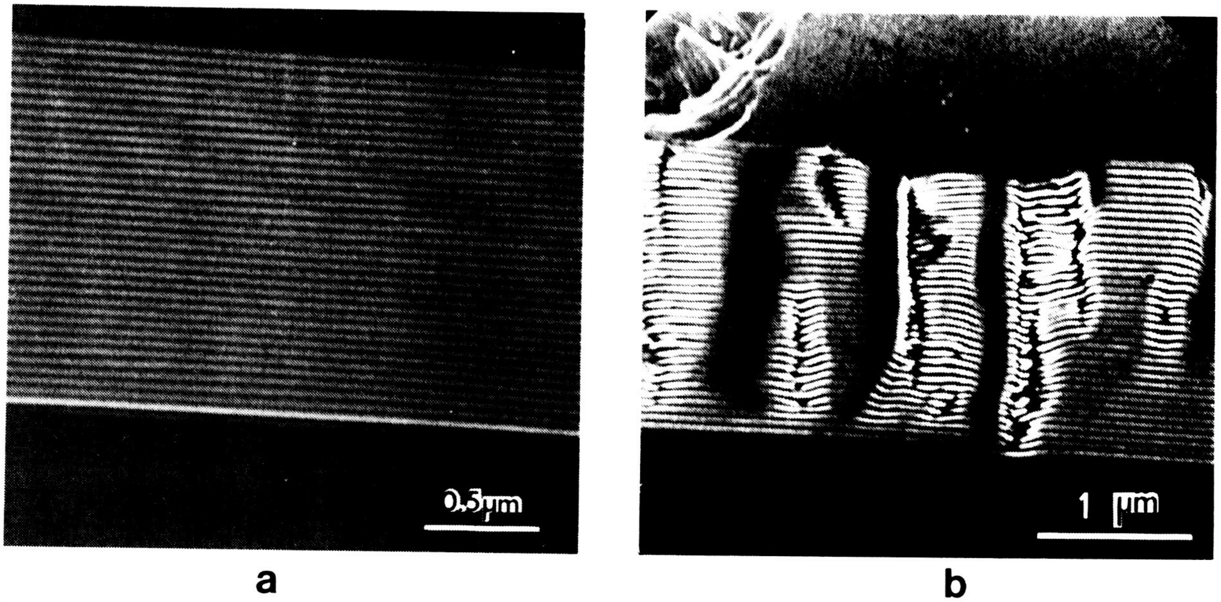

Figure 1. SEM photographs of cleaved and etched superlattice structures illustrating the effect of Δf (misfit) on superlattice morphology: (a) $GaAs_{.75}P_{.25}/GaAs_{.65}P_{.35}$; (b) $GaAs_{.80}P_{.20}/GaAs_{.60}P_{.40}$.

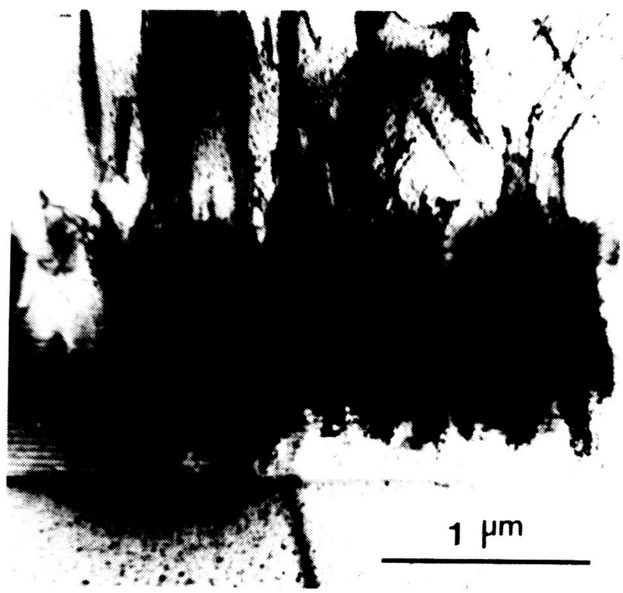

Figure 2. Cross-sectional TEM view of distorted superlattice. The black patches are phosphorus-rich regions and the lines emanating from them are dislocations.