

Comment on "Delayed Relaxation by Surfactant Action in Highly Strained III-V Semiconductor Epitaxial Layers"

A recent Letter by Grandjean, Massies, and Etgens on the use of surfactants to inhibit three-dimensional island formation in InAs/GaAs(100) heteroepitaxy [1] brings to light some important issues with regard to the primary function of a surfactant in affecting the growth mode of films growing in a so-called "Stranski-Krastanow" (SK) mode. The claim by Grandjean [1] and others previously [2] is that by reducing the surface free energy of a strained overlayer using a surfactant, the growth mode may be altered (i.e., islanding suppressed). We wish to point out that for the SK mode, where beyond the wetting monolayers growth is A on strained A , lowering the surface free energy actually facilitates island formation. This can be understood by considering that forming an islanded film (for SK growth it is energetically favorable for islands to form on the wetting monolayers rather than on the substrate) increases the surface area of the overlayer. Thus, by lowering the surface tension, there is relatively less energy cost associated with forming a three-dimensional islanded microstructure. On the other hand, by increasing the surface free energy of the overlayer, islanding becomes more energetically costly. In the InAs/GaAs(100) system, we have recently demonstrated (without using a surfactant) that increasing the surface tension of the overlayer will inhibit island formation [3]. It appears then that having only surface tension as a parameter to control the SK growth mode, it should be large in order to achieve planar growth. This is in contrast to Volmer-Weber growth, where planar growth of the first monolayer (i.e., wetting) could be achieved by decreasing the surface free energy of the epilayer.

With regard to segregation, it is implicit in Grandjean's argument that lowering the overlayer surface free energy is necessary in order that In and As atoms will prefer exchanging sites with the Te surfactant atoms and be incorporated into subsurface sites. A problem arises because surface free energy is a macroscopic term, and as has previously been suggested [4], the exchange and incorporation is a local process. In such a situation, it is only necessary that on the scale of a few atoms the local configuration which is energetically favored is that with the surfactant atoms at the surface rather than embedded. The likelihood that newly deposited film atoms vertically exchange sites with surfactant atoms will depend on the energy difference between the two configurations (i.e., the driving force). Although, on a macroscopic

scale, lowering the surface tension of the bare film may be an accompanying effect, it need not be.

It is stated by Grandjean, Massies, and Etgens that by reducing surface diffusion kinetics of film atoms, islanding may be suppressed. We believe this is the relevant physical effect enabling surfactants to dramatically alter the growth mode. Once an overlayer atom is subsurface, diffusion may be significantly reduced. This is because the energy barrier for thermally activated hopping may be increased by the surfactant. The important point is that the barrier is determined in a complex way by the local atomic configuration, not surface free energies. Thus, the success of surfactants is due to altering kinetics, not energetics as has been previously suggested. Indeed, we have demonstrated (without using surfactants) that reducing surface diffusion kinetics will alter the growth mode and suppress island formation in highly strained InGaAs/GaAs(100) [5]. However, by using surfactants one may reduce surface diffusion without lowering the temperature.

In our view, a surfactant segregates and produces an increased energy barrier for hopping. This reduces surface diffusion, thus inhibiting island formation. Lowering surface tension in previous cases has been an accompanying effect, but island suppression was not due to this. It might be argued that by definition a surfactant lowers the surface free energy of the overlayer. However, from this definition, it does not follow that lowering the surface free energy of the overlayer is central to inhibiting island formation. This being the case, perhaps the community should consider an alternate term to "surfactant."

C. W. Snyder and B. G. Orr

Harrison M. Randall Laboratory of Physics
The University of Michigan
Ann Arbor, Michigan 48109-1120

Received 31 August 1992

PACS numbers: 68.55.Bd, 61.14.Hg, 68.35.Bs

- [1] N. Grandjean, J. Massies, and V. H. Etgens, *Phys. Rev. Lett.* **69**, 796 (1992).
- [2] M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, *Phys. Rev. Lett.* **63**, 632 (1989).
- [3] C. W. Snyder, H. Munkata, and B. G. Orr, *Appl. Phys. Lett.* **62**, 46 (1993).
- [4] R. M. Tromp and M. C. Reuter, *Phys. Rev. Lett.* **68**, 954 (1992).
- [5] C. W. Snyder, J. Mansfield, and B. G. Orr, *Phys. Rev. B* **46**, 9551 (1992).