Self-organized superlattice formation in II−IV and III−V semiconductors

Albert-László Barabási[a)]

Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

There is extensive recent experimental evidence of spontaneous superlattice (SL) formation in various II−VI and III−V semiconductors. Here we propose an atomistic mechanism responsible for SL formation, and derive a relation predicting the temperature, flux, and miscut dependence of the SL layer thickness. Moreover, the model explains the existence of a critical miscut angle below which no SL is formed, in agreement with results on ZnSeTe, and predicts the formation of a platelet structure for deposition onto high symmetry surfaces, similar to that observed in InAsSb. © *1997 American Institute of Physics.* [S0003-6951(97)03806-0]

The design and growth of superlattices (SLs) with optimal electronic, magnetic, and optical properties is a challenging problem, with major applications for the production of electronic and optical devices. In this light, recent experimental evidence on spontaneous (or self-organized) SL formation[1−3] opens new, still largely unexplored ways for creating new materials with potentially important electronic properties.

Spontaneous SL formation has been observed in several III−V and II−VI materials, including InAsSb, GaAsSb, ZnSeTe, and ZnCdSeTe. In the $ZnSe_{1−x}Te_x$ system, Zn, Se, and Te were *simultaneously* deposited on a vicinal GaAs(001) substrate.[1,2] Transmission electron microscopy and x-ray scattering revealed spontaneous formation of modulated composition x along the growth direction, leading to a layered structure of varying Se and Te rich regions of thickness with a surprisingly regular period that varied between 18 and 32 Å in various specimens. Interestingly, no SL was observed to form for miscuts smaller than 4°. In contrast to this, InAsSb grown on high symmetry [001] surfaces resulted in anisotropically shaped interleaved platelets of two different alloy compositions,[3] with thickness varying between 240 and 500 Å. In addition to these two well investigated systems, natural SLs have also been observed in GaAsSb and ZnCdSeTe.[4]

It is well established that tetrahedrally bonded semiconductor alloys grown by epitaxy frequently exhibit spontaneous departures from a purely random distribution of their constituents. Specifically, formation of *atomic* superlattices along various crystallographic directions and/or phase separation have been observed and studied in practically all III−V and several II−VI systems.[5] However, the self-organized superlattices discussed here differ from atomic ordering in that it is *mesoscopic* in scale, and the period of the SL is not an integer multiple of the lattice constant. Closest to this behavior is phase separation, consequently this phenomena is often called *vertical phase separation*.[5]

For device applications we must be able to control the period of the SL. As a first step in this direction, here we propose an atomistic mechanism that sheds light into the dynamics of spontaneous SL formation and allows us to predict the temperature, flux, and miscut angle dependence of the layer thickness. Moreover, the model can account for the minimal miscut angle observed in the II−VI materials, and predicts the T and F dependence of this angle, where T is temperature and F is the deposition flux in ML/s. In the absence of a miscut the model predicts the development of elongated platelets, in accord with the experimental observation for III−V materials.

The existence of a minimal miscut for ZnSeTe indicates the key role which the steps play during growth, strongly suggesting that the growth mode is what is referred to as *step flow*, i.e., island nucleation on terraces is negligible. Indeed, the nucleation of Se or Te rich islands on the steps would eventually destroy the long-range order. However, SL formation implies that there is a preferential bonding of the Se(Te) atoms to the Se(Te) rich steps. Since in the zinc blende lattice there is no direct bond between the Se and Te atoms (neither direct Se−Se or Te−Te bonds), the information about the chemical composition has to be transmitted through stress and stress-generated lattice distortions.[6] Such preferred bonding is the result of the composition and strain induced free energy changes that are much studied for (mostly III−V) semiconductor materials, often leading to clustering and phase separation.[5,7]

Growth model. We have the following model for the SL formation (see Fig. 1). Zn, Se, and Te are deposited simultaneously on a vicinal surface, where they diffuse. The interface grows in a step-flow mode. Te (Se) diffuses on the surface, seeking a step rich in like atoms, i.e., Se wants to attach to the edge of a terrace made up of mostly Se atoms, and likewise for Te. Once it finds such a step, we consider that it sticks instantaneously (we shall return to this assump-
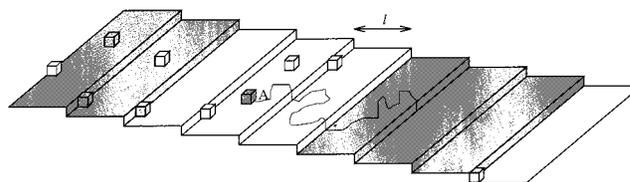

FIG. 1. The mechanism of superlattice formation in the ZnSeTe system. The Te atoms (gray) want to attach to the edge of Te rich steps, and Se (white) atoms attach to the edge of the Se rich steps. Thus the deposited adatoms need to travel a certain distance before they are able to find the step edge where they can attach. The Te atom (A) can either aggregate with other Te atoms and nucleate a new Te island on the Se step, thus destroying the long-range order in the system, or it can diffuse (continuous line) until it reaches a Te step edge, where it sticks. For SL formation the diffusion length of the Te atom has to be larger than the average distance it needs to travel to reach a Te step.

[a)]Electronic mail: alb@nd.edu

tion below). The Zn atoms may also diffuse on the surface, being trapped as they find two Se and/or Te bonds. However, Zn diffusion is not relevant for the present model, since the Zn composition is not modulated experimentally.

It is energetically most desirable for the system to grow thick stress-free ZnSe or ZnTe layers. For this to happen the adatoms must have a very long diffusion length to reach the distant preferred step. However, the adatoms (Se and Te) have a finite time to diffuse before being ''buried'' by the freshly deposited atoms. Thus the period of the SL is limited by the ability of the Se and Te atoms to reach such preferred step sites: the further the atoms can diffuse in the time available for diffusion, the larger is the period of the SL.

SL layer thickness. The mechanism for SL formation, outlined above and shown in Fig. 1, can be formulated quantitatively, allowing us to predict the period of the SL. If the SL has a period of N monolayers (ML), the *average* distance a Te atom needs to travel to reach a Te (Se) step edge is proportional to the total length of N steps, $d \sim N\ell$, where ℓ is the length of a single step, given by $\ell = a/\tan\alpha$, and a is the height of a single step. Assuming that the atoms follow a Brownian trajectory, the average time, τ, needed for the diffusing atom to reach the step is given by $d^2 \simeq D\tau$, where D is the diffusion constant. Here we assume that Se and Te have the same diffusion constant, i.e., $D_{Se} = D_{Te} = D$. If $D_{Se} \neq D_{Te}$, then the smaller diffusion constant determines the period of the SL.

The adatoms must attach to their preferred step edge before being buried by the incoming adatoms. The average lifetime of an adatom is given by the time necessary to deposit a full monolayer of atoms, i.e., $\tau = 1/F$. Combining these, we find

$$N \simeq \frac{\tan\alpha}{a}\left(\frac{D}{F}\right)^{1/2}. \tag{1}$$

It is known from the theory of surface diffusion[8] that

$$D = D_0 \exp\left[-\frac{E_d}{k_B T}\right], \tag{2}$$

where E_d is the activation energy for surface diffusion of the adatoms and D_0 is the surface diffusion constant.[8] Combining Eqs. (1) and (2) we obtain

$$N \simeq \left(\frac{D_0}{F}\right)^{1/2}\frac{\tan\alpha}{a}\exp\left[-\frac{E_d}{2k_B T}\right], \tag{3}$$

which provides the temperature-flux-miscut dependence of the SL period. Technically Eq. (3) provides the *largest* SL period allowed by diffusion. However, to decrease its strain energy the system wants to grow as thick as possible ZnSe or ZnTe layers, this tendency being limited only by diffusion, making the largest allowed period (3), the actual period of the SL.

The attachment of the atoms to like steps is a probabilistic process, thus there is a nonzero probability that Se atoms would attach to a ZnTe step, even though such bonding is energetically less favorable than bonding to the ZnSe step. This makes the transition observed between the Se and Te rich region blurred, allowing for a gradual change in the

composition. Indeed, x-ray diffraction data on the ZnSeTe system indicate the presence of a sinusoidal profile along the growth direction.[1]

Critical miscut angle. The experimentally observed lower cutoff in the miscut angle (critical miscut)[1] follows naturally from the model of Fig. 1: at small miscuts ℓ is large and the adatoms do not have the necessary time to reach the edge of the terrace before they are clamped by the arrival of new atoms. In this case we witness *island* nucleation at the surface of the terrace. Since in the vicinity of a ZnSe step Se is captured by the step, most likely a ZnTe island is nucleated, ending the long-range order. Thus the critical miscut angle is the smallest miscut for which island formation is still inhibited.

To evaluate the temperature and flux dependence of this smallest miscut we need to connect the typical length scale in the system (for instance, the typical distance between the islands) to the flux as if there were no steps on the surface. To make progress, we use the properties of random walks on a plane, assuming that only monomers are mobile. This question has been addressed in the context of submonolayer epitaxy, providing the characteristic length scale as[9,10]

$$\ell_d \sim \left(\frac{D}{F}\right)^{\psi_d}, \tag{4}$$

with $\psi_d = 1/6$. In deriving $\psi_d = 1/6$ it is assumed the dimers are stable and that the generated islands are not fractal. For extensions of these results to other cases, including the possibility of a nonzero critical nucleus, see Refs. 9 and 10.

When the typical distance between the islands, ℓ_d, is smaller than the terrace size, ℓ, island formation is observed on the top of the terraces, destroying the long-range order which characterizes the SL. When $\ell_d > \ell$, the atoms are captured by the edge of the steps, and no island nucleation is expected. The condition for island formation, $\ell_d < \ell$, leads then to the critical miscut angle

$$\tan\alpha_c \simeq \left(\frac{F}{D_0}\right)^{\psi_d}\exp\left[\frac{\psi_d E_d}{k_B T}\right]. \tag{5}$$

Comparison with experiments. We can use Eqs. (3) and (5) to compare experimental values of the period N measured at different miscuts, temperatures, and fluxes. The only unknown is the diffusion energy, that we take to be $E_d = 0.5$ eV. As a first application we calculate the expected variation in the period of ordering as the *flux and miscut are kept fixed* and the *temperature is varied* between the experimentally used values, 275 and 350°C. From Eq. (3) we find $N(T_2)/N(T_1) = 1.89$, i.e., increasing the temperature between these limits doubles the period of the SL. If we keep the *temperature and miscut constant* and *increase the flux* from $F_1 = 2.5$ Å/s to $F_2 = 3.5$ Å/s, the period should decrease by a factor $N(F_2)/N(F_1) = (F_1/F_2)^{1/2} = 0.84$. While the precise temperature and flux dependence of the SL modulation periods is not known yet, we can compare these predictions with the reported variation in the period as the experimental parameters were varied. Between the mentioned temperature and flux limits the experimentally measured layer thickness

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varied between 18 and 32 Å,[1] i.e., a factor of 1.77, in good quantitative agreement with the previous predictions.

We can also calculate the expected variation in the critical miscut angle as the growth parameters are varied. For the temperature range discussed above, we find $\tan\alpha_c(T_2)/\tan\alpha_c(T_1)=0.76$, while for the experimental flux range we obtain $\tan\alpha_c(F_2)/\tan\alpha_c(F_1)=(F_2/F_1)^{1/6}=1.057$, i.e., for the temperature and flux ranges used during the growth, α_c varies only slightly (20% within the temperature window, and 5% with the flux). This explains the experimentally observed stability of α_c: the previous predictions indicate that under the growth conditions used α_c is practically independent of the growth parameters.

Platelet formation and SLs in III–V semiconductors.[3] The previous discussion underlies the importance of the miscut in self-organized SL formation. In the absence of a miscut the stabilizing effect of the steps is absent, and the system cannot grow in a step-flow mode. Thus, Eq. (3) is no longer valid. In this case, one expects island formation on the surface. However, if the same stress-induced affinity exists for As to attach to InAs islands and Sb for InSb islands, this would result in the segregation of InSb and InAs elongated islands, or platelets, with typical horizontal size ℓ_d. Indeed, detailed evidence about such platelets is presented for InAsSb grown on high symmetry surfaces.[3] Moreover, the anisotropic nature of the platelets (they have different sizes along the $[110]$ and $[\bar{1}10]$ directions) indicate the anisotropy in the energy barriers (E_d) for adatom diffusion along the two principal surface directions. Also, in the light of the discussed mechanism, SL formation may be induced by the development of local slopes on the surface as a result of the kinetic roughening of the growing surface.[10] Whether such slopes facilitate the development of the superlattices in InAsSb is an open question. However, for ZnSeTe, even under growth with zero miscut, small domains of self-organized SLs have been observed,[4] most likely being correlated with the roughening of the surface, and the resulting local slopes with inclination larger than α_c.

In conclusion, we presented a mechanism for spontaneous SL formation that allows us to explain both the SL observed in the II–VI materials, and the platelets observed in the III–V systems. For growth on vicinal surfaces we can also predict the dependence of the SL period on the experimental parameters, that can be directly tested by further experimental work, and can guide the growth of the SLs for potential device applications. Furthermore, the model can explain the origin of the lower cutoff in the miscut angle, and its relative stability within the used experimental conditions. The understanding of the mechanism responsible for SL formation may also help in identifying other materials for which self-organized SL formation is possible.

[1] S. P. Ahrenkiel, S. H. Xin, P. M. Reimer, J. J. Berry, H. Luo, S. Short, M. Bode, M. Al-Jassim, J. R. Buschert, and J. K. Furdyna, Phys. Rev. Lett. **75**, 1586 (1995).

[2] S. P. Ahrenkiel, Ph.D. thesis, University of Colorado, 1995.

[3] A. G. Norman, T.-Y. Seong, I. T. Ferguson, G. R. Booker, and B. A. Joyce, Semicond. Sci. Technol. **8**, S9 (1991); I. T. Ferguson, A. G. Norman, T.-Y. Seong, R. H. Thomas, C. C. Phillips, X. M. Zhang, R. A. Stradling, B. A. Joyce, and G. R. Booker, Appl. Phys. Lett. **59**, 3324 (1991).

[4] J. Furdyna (unpublished).

[5] A. Zunger and S. Mahajan, in *Handbook of Semiconductors*, edited by T. S. Moss and S. Mahajan (Elsevier, New York, 1994).

[6] M. R. Weidmann and K. E. Newman, Phys. Rev. B **51**, 4962 (1995); K. E. Newman, J. Shen, and D. Teng, Superlattices Microstruct. **6**, 245 (1989).

[7] I. P. Ipanova, V. G. Malyshikin, and V. A. Shchukin, J. Appl. Phys. **74**, 7198 (1993).

[8] T. T. Tsong, Rep. Prog. Phys. **51**, 759 (1988).

[9] J. Villain, A. Pimpinelli, and D. Wolf, Comments Condens. Matter Phys. **15**, 1 (1992); S. V. Ghaisas and S. Das Sarma, Phys. Rev. B **46**, 7308 (1992).

[10] A.-L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995).