Kinetic approach to dislocation bending in low-mobility films

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A kinetic model has been developed for dislocation bending at the growth surface in compressively stressed low-mobility films such as III-V nitrides. It is based on a reduction in the number of atoms at the growth surface. Stress and nonstress sources of driving force for such a reduction are discussed. A comparison between the derived equations and experimentally measured stress evolution data yields good agreement between the predicted and observed angles through which dislocations bend.

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The group III-A nitrides are of importance for light-emitting diodes, laser diodes, and high-power, high-frequency electronic applications. Owing to the lack of native substrates, III-nitride films are grown heteroepitaxially. In-built growth stress and threading dislocations are a common feature of such heteroepitaxially grown films. During growth, stress evolution and dislocation structure evolution occur simultaneously and are interdependent.[1–3] Because both stress and threading dislocation densities affect film properties and device performance,[4] understanding this interrelationship is important.

Owing to poor surface and bulk diffusion at growth temperatures the III-nitrides are categorized as low-mobility films.[5] Also, the threading dislocations present in $\{0001\}$-oriented nitrides, the most common growth direction, are immobile owing to the lack of shear stresses on the basal planes. In such systems with poor atom and dislocation mobility, dislocation bending at the growth surface is one of the few routes available for stress relaxation.[1] In addition, if the threading dislocation lines are straight (line direction perpendicular to the substrate-film interface), bending is the only means of engendering interaction with neighboring dislocations.[6] Such interactions help reduce dislocation density, which is essential to improving the quality of current nitride devices.[7]

One way in which dislocation bending can help relax stresses is shown schematically in Fig. 1.[1,6,8] A straight threading dislocation is shown intersecting the growth surface at a point P in Fig. 1(a). The two rows of atoms shown belong to the nth and $(n-1)$th atomic layers from the film-substrate interface in the growth direction, z. Removal of atoms from the dislocation core would result in retraction, as shown in Fig. 1(b). Eventually, following a sequence of such events at different film thicknesses, the previously straight dislocation line would appear inclined, as shown in Fig. 1(c). A similar picture of dislocation inclination has been proposed by Follstaedt *et al.*,[8] though the mechanism proposed was not exactly as outlined above. Retraction requires a reduction in the number of atoms in the nth layer relative to the $(n-1)$th layer, which generates tensile stresses and hence relaxes compressive stresses. The horizontal segments created in the process are essentially misfit dislocation segments. In comparison, the addition of atoms at point P in Fig. 1(a) would result in the exact opposite, or dislocation advancement. It would create a horizontal misfit segment in the nth layer, and place it in relative compression with respect to the $(n-1)$th layer. Any existing tensile stress would be relaxed. Thus, bending should be able to generate and relax both tensile and compressive film stresses. However, in low-mobility III-nitride films grown at relatively fast rates, in excess of 1 Å/s, typically by chemical vapor deposition (CVD), dislocation line bending is only observed to relax compressive stresses[2,3,9] or generate tensile stresses.[1,7,8,10] Bending-induced tensile stress relaxation is not seen in such films.

Using a thermodynamic approach to explain relaxation in compressively stressed AlGaN films, Romanov and Speck first proposed that a dislocation would bend after stressed films attained a certain critical thickness.[1] Since then, many groups have reported the linear relationship between stress relaxation and film thickness predicted by the model for a constant angle of bending in compressively strained films.[8,10,11] However, there are many observations that cannot be rationalized using thermodynamics alone. For instance, if thermodynamics were the only hurdle, then dislocation bending should also be able to relax tensile stresses. However, in III-nitride films grown by chemical vapor deposition (CVD) at rates in excess of 1 Å/s, dislocation line bending is only observed to relax compressive stresses.[1–3,8,9] Also, although not implied by the Romanov-Speck model above, implicit in critical-thickness thermodynamic models is the assumption that dislocation bending can occur behind the growth front. This would require bulk diffusion to the dislocation cores. However, experiments have shown that bulk diffusion at growth temperatures $<1100\,^{\circ}$C is negligible in nitrides.[12,13] This view is also supported by the fact that dislocation configurations in compressively stressed nitrides remain "frozen in."[8] In addition, recent experimental data[8] on the critical thickness for the onset of bending is in disagreement with the thermodynamic treatment. To address these inconsistencies, a kinetic approach is used in this Brief Report to model processes occurring at the growth surface. It is then used to correlate dislocation bending with compressive stress relaxation. The kinetic reasons for the lack of relaxation by dislocation bending in films stressed in tension is discussed at the end.

A schematic of the mechanism being proposed and modeled is outlined in Fig. 2. It is restricted to the growth surface, implying that all process cease in the nth layer once the $(n+1)$th layer is deposited over it. A straight dislocation intersects the growth surface at point P in the nth layer. A nuclei corresponding to the $(n+1)$th layer is also shown. For the dislocation to bend, atoms at the dislocation core need leave (or join) the nth layer. It is proposed that this process occurs in the nth layer until the point of intersection with the growth surface is swept over and buried under the advancing

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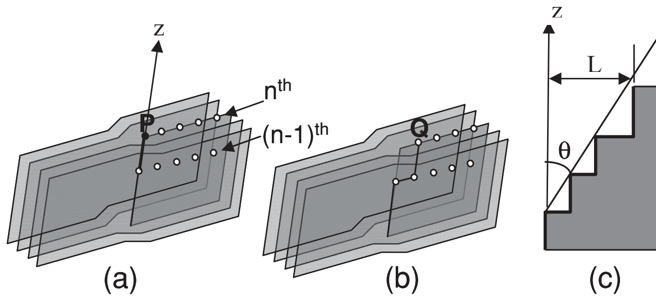

FIG. 1. Dislocation bending owing to removal of atoms from the dislocation core. (a) A threading dislocation is normal to and intersects the growth surface at P in the nth layer from the film-substrate interface. The growth direction is given by z and atomic rows belonging to the nth and $(n-1)$th layers are shown. (b) Removal of the filled circle at point P in (a) results in retraction from P to Q in the nth layer, and the deposition of a horizontal misfit segment, in the $(n-1)$th layer. Such removal and retraction leaves the nth layer in relative tension to the $(n-1)$th layer. The opposite, an addition of atoms, would result in a misfit segment in the nth layer and leave it in relative compression to the $(n-1)$th layer. (c) A sequence of such events results in "retraction" of the dislocation plane and inclination of the line to the growth direction, z, at an angle θ. Formation of 90° steps has also be proposed by Follstaedt *et al.* (Ref. 8), while Romanov and Speck (Ref. 1) have considered steps inclined at all angles. Dislocations would "progress" or incline in the opposite direction to the one shown in (c) when atoms are added to the core.

step constituting the $(n+1)$th layer. Further bending then continues in the $(n+1)$th layer.

In this Brief Report, the change in the number of atoms required for dislocation bending is modeled as a diffusion of atoms into (for compressive stress generation) or out of (for tensile stress generation) the dislocation core at the growth surface. In the case of the III-V nitrides under consideration, following Chason *et al.*,[14] the outdiffusion required for dislocation retraction is expressed by a kinetic equation of the form

$$\frac{dN}{dt} = \rho_{\mathrm{TD}}\,(C\Gamma)^{o}\,[1-\exp(-\Delta\mu/kT)]. \tag{1}$$

dN/dt is the rate of atom removal from the growth surface per unit area, ρ_{TD} is the threading dislocation density, $(C\Gamma)^{o}$ is the number of atoms leaving a single dislocation core per second, $\Delta\mu$ is the driving force for such diffusion, and T is the growth temperature. $\Delta\mu$ is the difference between the chemical potential of the atoms in the growth front at the dislocation core of the stressed film and the chemical potential of the perfect, unstressed crystal surface at equilibrium.

Typically, film growth by CVD is carried out at values of global supersaturation that is large enough to deposit a highly stressed and highly defective film. Hence, the average chemical potential existing on the growth surface would be one that drives adatoms to join the growing surface and not to leave it. This is a necessary condition for net film growth. Thus, the driving force for outdiffusion, $\Delta\mu$ in Eq. (1), from the stressed dislocation cores must be in response to local undersaturation on the growth surface. One mechanism by which such local undersaturation could occur is as follows. Steps on the growth surface act as sinks for adatoms. Thus, as a step belonging to the $(n+1)$th layer in Fig. 2 nears the point of intersection P, the local concentration of adatoms would be lower at the step edge than away from it. If the growth surface at this point became undersaturated with respect to the chemical potential of the atom sitting at the stressed dislocation core, it would drive atoms out of the already formed nth layer and possibly also the $(n+1)$th being formed. An increase in roughness or a higher step density of the growth surface, a lower surface mobility, and the presence of chemical species that lower the surface chemical potential would aid the process.

Experimental evidence suggests that there could be three components that contribute to the local undersaturation. They are stress, σ, reactor chemistry (RC), and dislocation interaction (DI). Hence, it is proposed that $\Delta\mu$ in Eq. (1) be expressed as

$$\Delta\mu = -\sigma\Omega + \Delta\mu_{\mathrm{RC}} + \Delta\mu_{\mathrm{DI}}. \tag{2}$$

Ω is the atomic volume. Hence, the first term $\sigma\Omega$ in Eq. (2) is the stress-related driving force. A compressive stress, $\sigma < 0$, would drive atoms out of the interface, whereas a tensile stress would favor the incorporation of atoms into the interface. The stress being referred to here is the incremental stress calculated from the slope of the stress-thickness versus thickness plots. In low-mobility systems such as nitrides, where all other diffusional relaxation mechanisms are nonexistent, the incremental stress can be equated to the stress at the growth surface. (See Table I for a list of data used.)

If compressive stress were the only driving force for outdiffusion, then dislocation bending would only relax stresses to zero. However, the data obtained by *in situ* measurements of stress during growth of undoped and Si-doped AlGaN by Acord *et al.*[10] and Manning *et al.*[7] point to the contrary. As can be seen from Fig. 3, the initial compressive stress does not just decrease to zero, but transitions to a net tensile stress. The tensile stress then saturates at an eventual steady-state value. The final steady-state tensile stress is seen to be dependent on reactor chemistry—in their case an increase in silane partial

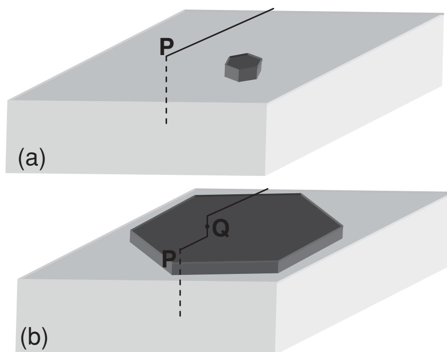

FIG. 2. Bending at the surface during growth. (a) A threading dislocation intersects the growth surface at P in the nth layer. A random nucleus corresponding to the $(n+1)$th layer is also shown. (b) By the time the nucleus grows laterally and sweeps past the threading dislocation, the dislocation has retracted to point [represented by the dot in (b)] Q in the nth layer. This point Q remains frozen in in the nth layer. The misfit segment of length equal to that of PQ is in the $(n-1)$th layer. Further retraction will then be restricted to the $(n+1)$th layer.

TABLE I. Data used.

$\Omega = 2 \times 10^{-29}$ m^3	$k = 1.38 \times 10^{-23}$J/K	$R = 0.6 \times 10^{-9}$ m/s[10]
$M_{\mathrm{GaN}} = 470$ GPa	$M_{\mathrm{AlN}} = 510$ GPa	
$a_{\mathrm{GaN}} = 3.19 \times 10^{-10}$ m	$a_{\mathrm{AlN}} = 3.11 \times 10^{-10}$ m	$N_o = 7 \times 10^{18}/\mathrm{m}^2$

pressure used for Si doping—from values as low as 0.08 GPa for undoped films to 2.3 GPa for films doped with 2.5×10^{19} atoms/cm^3 of Si. These two extreme cases are plotted in Fig. 3. The stress evolution from an initial compressive stress to a final steady-state tensile stress is accompanied by bending of dislocations. Similar results have been reported by other groups[1,8,15] as well. Thus, these experimental observations prove conclusively that nonstress sources of driving force for outdiffusion must exist. The $\Delta\mu_{\mathrm{RC}}$ term in Eq. (2) represents the component that is dependent on RC. It would be constant for a given set of growth conditions. Hence, in the absence of other sources as discussed below, when tensile stress, which opposes outdiffusion, at the growth surface reaches a value such that $\Delta\mu_{\mathrm{RC}} - \sigma\Omega = 0$, dislocation bending would cease. Film growth would continue at the steady-state value given by $\sigma = \Delta\mu'_{\mathrm{RC}} = \Delta\mu_{\mathrm{RC}}/\Omega$. It would be a function of RC, as reported by Manning *et al.*[7] and as seen in Fig. 3. The physical origins of $\Delta\mu_{\mathrm{RC}}$ remain beyond the scope of this Brief Report, whose main aim is to suggest a kinetic approach to the problem of dislocation bending. However, surface roughness, currently under debate,[7,8,16] could be a potential source.

Last, the $\Delta\mu_{\mathrm{DI}}$ term in Eq. (2) accounts for any additional driving force that comes from the interaction between dislocation cores that satisfy the b^2 criterion for reduction in energy. This term would have to be considered if the kinetic model were to be used for explaining stress evolution in GaN films, wherein extensive dislocation interaction and density reduction (approximately two orders of magnitude) along

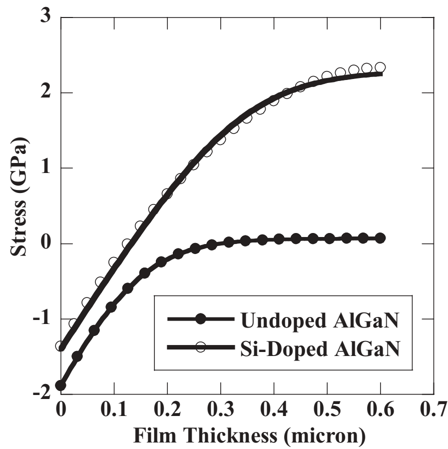

FIG. 3. Fit (solid line) of experimental data (solid and filled circles) with Eq. (4) to yield $\rho_{\mathrm{TD}}(C\Gamma)^o$. The data points, incremental stress values, were obtained from the slope of the stress thickness vs thickness plots reported by Acord *et al.* (Ref. 10) and Manning *et al.* (Ref. 7) from *in situ* stress measurements for undoped and doped AlGaN, respectively. The slope yields the stress at the growth surface in films where the change in curvature is only owing to the addition of new stressed material and all other relaxational processes can be neglected.

with tensile stress generation[2] is observed. Such interaction occurs when the cores are within a certain interaction distance, ∼500 Å for nitrides.[17] In the AlGaN system being considered here, even though dislocation interaction and density reduction are observed,[7] dislocation bending is the predominant microstructural evolutionary feature. Hence, ρ_{TD} will be assumed to be a constant and $\Delta\mu_{\mathrm{DI}}$ will be neglected henceforth. Errors introduced owing to this assumption will be discussed later.

Following Sheldon *et al.*,[13] the rate of stress relaxation with respect to film thickness can be related to the rate of atom reduction as

$$\frac{d\sigma}{dz} = \frac{M}{R}\left(\frac{1}{N_o}\frac{dN}{dt}\right). \tag{3}$$

Here, M is the biaxial modulus, $R = dz/dt$ is the growth rate along the z direction, and N_o is the number of atoms per unit area of the surface. The term in the parentheses is the rate of strain generation. Using Eqs. (1)–(3) and integrating with initial conditions $z = 0$ and $\sigma = \sigma_i$ yields

$$\sigma(h) - \Delta\mu'_{\mathrm{RC}} = \frac{-1}{\beta}\ln(1 + \{\exp[-(\sigma_i - \Delta\mu'_{\mathrm{RC}})\beta] - 1\} \times \exp[-\alpha(C\Gamma)^o\rho_{\mathrm{TD}}h]). \tag{4}$$

Here, $\beta = \Omega/kT$, following the notation used by Sheldon *et al.*,[13] $\alpha = M\beta/RN_o$, and h is the film thickness. As mentioned before, $\Delta\mu'_{\mathrm{RC}}$ is the value of the final steady-state stress that would be observed depending on the value of $\Delta\mu_{\mathrm{RC}}$ existing at the growth surface. The actual film stress would, however, be limited by relaxation processes such as cracking if required thermodynamic fracture criteria were met, as discussed by Sheldon *et al.*[18]

Finally, the rate of horizontal segment [such as in Fig. 1(c)] formation, L [see Fig. 1(c)], with film thickness can be related to the rate of reduction in number of atoms as

$$\frac{dL}{dz} = \left(\frac{1}{\rho_{\mathrm{TD}}}\frac{dN}{dz}\right)\frac{a\sqrt{3}}{2}. \tag{5}$$

The first term in the parentheses is the rate of removal of atoms per dislocation core and the second term is the magnitude of retraction per atom. This comes from the fact that the a-type dislocation recedes by $a\sqrt{3}$, a being the lattice parameter, when two atoms leave the growth surface.[8] A simpler approximation would be the use of $\Omega^{1/3}$ instead. The angle through which dislocations bend is equal to $\tan^{-1}(dL/dz)$. Hence, from Eqs. (1) and (5) we get

$$\tan\theta = \frac{1}{R}\left[\frac{(C\Gamma)^o}{2}a\sqrt{3}\right]\left[1 - \exp\left(\frac{\Omega(\sigma - \Delta\mu'_{\mathrm{RC}})}{kT}\right)\right]. \tag{6}$$

Here, $\sigma - \Delta\mu'_{\mathrm{RC}}$ is not a constant but a function of thickness. Thus, Eq. (6) predicts that the angle of bending will change with thickness. A growth-rate effect should also be observed. At large values of net compressive stress, the term in the exponent becomes negligible and the maximum bend angle

would be $(C\Gamma)^o(a\sqrt{3})/2R$. Such angles would be observed close to the AlGaN/GaN interfaces. At large thicknesses, as the net stress tends to zero, as is also evident from Eq. (6), the process of outdiffusion should cease and so should dislocation bending (θ becomes zero). Thus, dislocations should take a bowed shape, as has been observed by Wang *et al.*[11]

The data in Fig. 3 is now analyzed by using Eqs. (4) and (6). The fits using Eq. (4) and 0.07 and 2.3 GPa for $\Delta\mu'_{\rm RC}$ are shown in Fig. 3. They yield values of 1.3×10^{14} and 1×10^{14}/s m^2 for the parameter $\rho_{\rm TD}(C\Gamma)^o$. Given that dislocation densities are of the order of $10^{14}/{\rm m}^2$, these estimates thus appears very reasonable. For the undoped AlGaN, using the experimentally determined[10] value of $4.5\times10^{14}/{\rm m}^2$ for the dislocation density, $(C\Gamma)^o$, which represents an upper bound on the rate at which atoms leave the growth surface at every dislocation, is now calculated to be 0.29/s. For an effective stress equal to -2.07 GPa (-2 GPa from growth stress and -0.07 GPa from undersaturation) at the beginning of growth the term in the exponent in Eq. (6) is 0.11, and it will become smaller as the compressive stress decreases. Using the experimentally determined value of 6 Å/s for R and 3.15 Å for the lattice parameter, Eq. (6) yields a value of 6.7° for the angle through which dislocations should bend at the beginning of growth, and a maximum bend angle in AlGaN films on AlN of 7.5°. The experimentally determined transmission electron microscopy (TEM) value by Acord *et al.* is 9.4 ± 6.6°, in fairly good agreement with the predictions of the model.

For Si-doped AlGaN it is seen that angles through which dislocations bend are, in general, larger. This in turn tends to engender greater interaction and hence density reduction.[7] Thus, a comprehensive treatment would have to include dislocation interaction as well. The larger bending angle [see Eq. (6)] can come from two sources: (1) The addition of silane could change the value of $(C\Gamma)^o$ as energy barriers to outdiffusion would be expected to be sensitive to changes in the reactor and hence surface chemistry. (2) Even for the same value of $(C\Gamma)^o$, the presence of an additional effective stress in the form of $\Delta\mu'_{\rm RC}$ in Eq. (6) implies that bending angles will be larger. A similar fitting exercise, as was done for the undoped AlGaN, yielded a value of 0.38 or 0.17 for $(C\Gamma)^o$ by using a value of 2.6 or $5.8\times10^{14}/{\rm m}^2$, respectively, for the range of ρ_{TD} reported.[7] For an effective stress value of -3.3 GPa (-1 GPa growth stress and -2.3 GPa owing to undersaturation) this yields a bend angle of 9.5° and 4.3° for $(C\Gamma)^o$ values of 0.38 and 0.17, respectively. The experimentally observed values reported by Manning *et al.* are 14.9 ± 7° and 16.28 ± 4.7°. The neglect of the dislocation interaction and the assumption of a constant dislocation density could be the two possible reasons for the lack of better agreement. It is pointed out that $\tan^{-1}(x)$ increases very sharply with x in the range of $x = 0$–1. Hence, very small errors in the measurement of dislocation density and hence estimation of $(C\Gamma)^o$ can have a significant effect of the predicted value of θ.

Last, the lack of bending-induced relaxation in CVD nitride films growing under a tensile stress is addressed using the kinetic framework. Tensile stress relaxation or compressive stress generation by dislocation bending requires an addition of atoms by surface diffusion to the threading dislocation cores. As proposed by Chason *et al.* and Sheldon *et al.*,[13,14] these processes become increasingly ineffective as growth rates are increased, as the rate of atom insertion cannot keep up with the rate of deposition of strained atomic layers. However, dislocation bending for tensile stress generation requires a reduction in the number of atoms. An atom sitting at the dislocation core just leaves its present location and hops onto the growth surface. Long-range diffusion is not required, and hence this process of tensile stress generation is expected to be active at growth rates higher than the one at which the compressive stress generation discussed previously becomes negligible.

In summary, a kinetic model has been developed to correlate dislocation bending and stress relaxation during growth of low-mobility films such as the III-V nitrides. The model describes the qualitative features of stress evolution with thickness in undoped and Si-doped AlGaN films very well. Good agreement is also observed between experimentally observed and theoretically predicted values of the angles through which dislocations bend for both undoped and Si-doped AlGaN films. The same model has been used also to explain the frequent observation that dislocations do not bend and relax tensile stresses at fast growth rates.

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