An approach to threading dislocation ''reaction kinetics''

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An approach is developed to describe the evolution of threading dislocation (TD) densities in lattice-mismatched epitaxial films. TD ensembles are treated in close correspondence to chemical species in chemical reaction kinetics. ''Reaction rate'' equations are derived for changing TD density with increasing film thickness for first- and second-order reactions. Selective area growth is an example of a first-order reaction. TD annihilation, fusion, and scattering are examples of second-order reactions. Analytic models are derived for TD behavior in relaxed homogeneous buffer layers, selective area growth, and strained layers. *© 1996 American Institute of Physics.* [S0003-6951(96)03348-7]

During the past 25 years a large body of research has been established on the theory and experiments for strain relaxation by misfit dislocations (MD) for lattice-mismatched epitaxial films (see, for example, the articles by Beanland *et al.*,[1] Freund,[2] and Fitzgerald[3]). In the growth of lattice-mismatched epitaxial thin films, threading dislocations (TDs) are concomitantly generated with MDs. For a wide variety of electronic and optoelectronic device applications, particularly for minority carrier devices, TDs are deleterious for physical performance. In recent years there has been substantial experimental effort to reduce TD densities. Despite the large literature to theoretically and experimentally understand critical thicknesses for MD generation, there have been relatively few theoretical efforts to understand the mechanisms in which TDs are eliminated in thin films.

Typically, for large mismatch films (e.g., mismatch strains in excess of $\sim 2\%$), the TD densities are quite high near the film substrate interface, often on the order of $10^{10}-10^{11}$ cm^{-2}. TDs are nonequilibrium defects that raise the free energy of the film. Thus, there is a thermodynamic driving force to diminish the TD density. The high densities of TDs facilitate the development of a kinetic approach for TD reduction; this treatment will be in close analogy to reaction kinetics for chemical systems (a similar approach has been used to describe plastic instabilities and dislocation pattern formation in bulk materials[4]).

In this letter, we present a new theoretical approach for understanding TD reduction in partially or fully strain relaxed films. The approach considers the reactions between TDs in relation to their densities and relative motion; this effectively is a ''reaction kinetics'' treatment. The evolution of TD ensembles is proposed to be associated with TD motion rather than time. The motion approach is used because during film growth, dislocation positions can be more easily measured than their velocities.

Relative TD motion may be achieved, for example, by changing layer thickness (e.g., growth of homogeneous buffer layers[5–7]) by the strain-driven migration of TDs to generate MDs in strained layer growth (''TD filters''[1]), or by point defect condensation.[8] The TD motion r, which is defined as the lateral movement of the intersection point of the TD with the free surface, may be written in the form

$$r = r(h, \epsilon_m, c), \tag{1}$$

where h is the film thickness, ϵ_m is the misfit strain between the film and substrate, and c is the nonequilibrium point defect concentration in the film. Changes in film thickness h give rise to lateral TD motion, as shown in Fig. 1(a). Misfit strain may lead to MD generation and concurrent TD motion, as shown in Fig. 1(b). A vacancy or interstitial supersaturation may lead to TD climb, as shown in Fig. 1(c). The extent of motion r in some cases should be modified to include its dependence on MD configurations and TD density itself, as during the growth of a partially relaxed layer [see Fig. 1(b)]. Thus, in general, r cannot be treated as a state variable.

Together with motion r, considered above, we treat the reactions that are associated with rapid processes when the

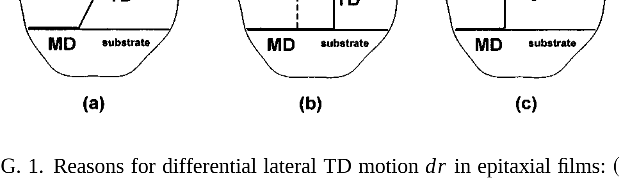

FIG. 1. Reasons for differential lateral TD motion dr in epitaxial films: (a) lateral motion of an inclined TD due to changing film thickness dh; (b) TD glide motion due to relaxation of misfit strain by MD formation; and (c) TD climb motion due to condensation of nonequilibrium point defects.

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separation of TD pairs is less than a reaction radius r_I. The reaction radius r_I represents the distance at which the interaction force between TDs is sufficient to overcome the Peierls barrier σ_p for TD glide or climb. Once initiated, this movement results in reaction and this is considered to be a fast process in comparison to motion r. r_I has the following dependence

$$r_I = r_I(\sigma_p, T, t, c). \tag{2}$$

In Eq. (2), it is assumed that temperature T, time t, and point defect concentration c, can all contribute to the change of the reaction radii either through thermally activated glide or point defect-assisted climb.

For chemical reactions, the reaction rate is determined by the concentration of reactants, the order of the reaction and, thus, the reaction mechanism, and the value of the rate constant k. We now make the analogy between chemical and TD ''reaction kinetics.'' The TD density ρ describes the reactant concentration. We consider here that the TD density is the number of TDs per unit area that cross a plane parallel to the film/substrate interface and, thus, ρ has dimension L^{-2} (where L is length). The order of a reaction corresponds to the type of reaction, that is, the number of elementary participants in the reaction, and we will deal mainly with reactions in which either one or two TDs will participate. For TDs, we are explicitly concerned with the mechanisms of motion that bring TDs within a reaction radius. The product of rate constant k with differential time dt, therefore, is equivalent to the product of the TD reaction parameter κ with differential motion dr (i.e., $k\,dt \leftrightarrow \kappa\,dr$). Therefore, for first- and second-order TD kinetics, we can write the following general equations:

$$\frac{d\rho}{dr} = \kappa_1 \rho; \tag{3}$$

$$\frac{d\rho}{dr} = \kappa_2 \rho \cdot \rho, \tag{4}$$

where κ_1 and κ_2 correspond to the first- and second-order TD reaction parameters with dimensions L^{-1} and L, respectively. Most experimental data for TD behavior are related to film thickness rather than time, thus, we usually attempt to relate differential TD motion dr with increasing film thickness dh.

The TD reaction parameter κ corresponds to the characteristic reaction length. In first order kinetics, TDs may either be generated and, thus, $\kappa_1 > 0$, or eliminated and, thus, $\kappa_1 < 0$, during TD motion. In the latter case, a length $\lambda = 1/\kappa_1$ may be introduced to characterize the average motion necessary for TDs to reach sinks such as mesa sidewalls in selective area growth. Second-order kinetics correspond to reactions between pairs of TDs. The possible reactions between TDs include *annihilation, fusion,* and *scattering*. In the current treatment, possible dislocation storage mechanisms, such as stable entanglement formation or node formation, are not included. Storage can give rise to saturation of TD densities and this possibility will be included in a future paper. In an annihilation reaction, TDs with opposite Burgers vectors that fall within an annihilation radius r_A react and stop the propagation of both TDs to the film surface. In a fusion reaction with a characteristic reaction radius r_F, two TDs react to produce a new TD with Burgers vector that is the sum of Burgers vectors of the reacting TDs. In a scattering reaction with a characteristic reaction radius r_S, the line direction and slip plane of one or both reacting TDs changes as a result of repulsive interactions. In a full treatment of the problem, crystallographic details and subdivision of the TDs into different populations (corresponding to specific Burgers vectors and line directions) must be included, however, we have demonstrated that when these details are incorporated, the total TD density obeys the general equations derived below.[9,10] For simplification here, we treat all reaction radii as a single parameter $r_I = -\kappa_2/2$.

Now we can describe the TD density evolution for some specific cases. Consider first the possibility of growing a relaxed buffer layer with finite lateral dimension as might be realized in selective area growth over a relaxed layer with high TD density. In this case, both first- and second-order kinetics will be included and the motion r is assumed only to depend on film thickness h, i.e., $r = r(h)$. For this case, the change in TD density with film thickness may be written as

$$\frac{d\rho}{dh} = -\frac{\rho}{\Lambda} - K\rho^2, \tag{5}$$

where $\Lambda = \lambda/G$, $K = 2Gr_I$, and $G = dr/dh$ is a geometric factor that describes TD motion during film growth and commonly $G \approx 1$ for inclined TDs in (001) cubic semiconductor films.[9] Equation (5) may be directly integrated to yield

$$\rho = \frac{\rho_0}{(1 + K\Lambda\rho_0)\exp[(h - h_0)/\Lambda] - K\Lambda\rho_0}, \tag{6}$$

where ρ_0 is the TD density at the initial thickness h_0. This solution has two asymptotes that are relevant for TD reduction. In the first limit, the mesa size is large in comparison with the film thickness, $\Lambda >> h - h_0$, and the solution corresponds to that for homogeneous buffer layers, i.e.,

$$\rho = \frac{1/K}{h + \hat{h}}, \tag{7}$$

where $\hat{h} = (\rho_0 K)^{-1} - h_0$. This is in agreement with experimental observations of TD density in homogeneous buffers.[5–7] As mentioned above, when the full crystallographic details for the TDs are included for (001) epitaxy of cubic semiconductors, Eq. (7) describes the global behavior for total TD density.[10] In the case that $\Lambda \to 0$, which is a limiting case of small mesas, there is exponential decay of TD density, i.e.,

$$\rho = \rho_0 \exp\left(-\frac{h - h_0}{\Lambda}\right). \tag{8}$$

The thickness dependence of TD density for both homogeneous buffer layers and selective area growth are shown in Figs. 2(a) and 2(b). For comparison, we also include preliminary results of computer simulations of the TD density in Fig. 2.[11] In the simulations, points representing TD intersections with a film surface were translated laterally as the film grows, according to prescribed TD trajectories in (001) ori-

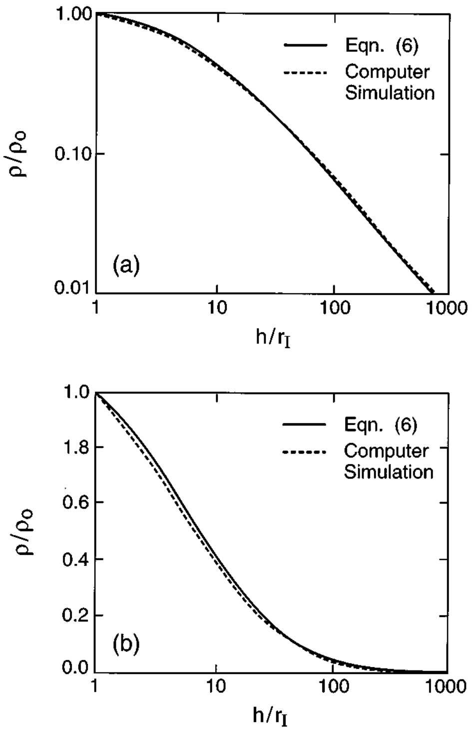

FIG. 2. The thickness dependence of TD density for (a) homogeneous buffer layers, i.e., in the limiting case where $\Lambda \gg h - h_0$, and (b) selected area growth over a relaxed layer for $\Lambda = 200 r_I$. For both (a) and (b), $\rho_0 K = 1/(7 r_I)$ and the geometric factor G was taken as unity.

ented face-centered-cubic semiconductor films. All pairs of TDs that fall within r_I are either removed (annihilation) or combined into a single TD (fusion).

For the analysis of TD behavior in intentionally introduced strained layers, we consider only the equilibrium relaxation by MD generation during film growth when the TD density is high (no sources of new TDs). For this model, blocking of TD motion by MDs[2,12] is neglected and the layer is laterally uniform. The equilibrium linear MD density ρ_{MD} (the number of MDs per unit length) at film thickness h is given as[13]

$$\rho_{\mathrm{MD}} = \frac{|\epsilon_m|}{b}\left(1 - \frac{h_c}{h}\right), \tag{9}$$

where h_c is the critical thickness and b is the magnitude of the TD Burgers vector. For increasing film thickness, the MD density ρ_{MD}, and thus length, increases by lateral motion of existing TDs. The average differential motion dr of a TD in the case of two-dimensional misfit is then given as

$$dr = \frac{2\epsilon_m}{b}\,\frac{h_c}{h^2 \rho(h)}\,dh. \tag{10}$$

Substitution of dr from Eq. (10) into the Eq. (2) for second-order kinetics leads to the following differential equation:

$$\frac{d\rho}{dh} = -B\,\frac{h_c}{h^2}\,\rho, \tag{11}$$

where $B = 4\epsilon_m r_I / b$. Equation (11) may be directly integrated to yield

$$\rho = \rho_c \exp\left[B\left(\frac{h_c}{h} - 1\right)\right], \tag{12}$$

where ρ_c is the TD density at the beginning of the strain relaxation process ($h = h_c$). For $h \gg h_c$, Eq. (12) predicts that the final TD density will diminish to $\rho_c \exp(-B)$.

In summary, we have modeled the evolution of TD densities in mismatched epitaxial films. The approach treats the behavior of TDs on the basis of reaction kinetics. Possible reactions between TDs are taken into account along with relative TD motion. We have shown analytic solutions for three methods of TD reduction of practical importance: homogeneous buffer layers, selective area growth, and strained layer growth. For homogeneous buffer layers, a $1/h$ dependence of TD density is predicted for large h, which is in close agreement with experimental data. For selective area growth, exponential decay of TD density is predicted. Finally, saturation behavior is predicted for strained layer growth.

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