Vacancy-controlled model of degradation in InGaAs/AlGaAs/GaAs heterostructure lasers

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A model is proposed for dark line defect (DLD) growth in semiconductor lasers by dislocation climb. The model assumes that climb occurs by the migration of randomly distributed vacancies toward existing dislocations. The effects of a strained layer on the number of vacancies and their stability are investigated. It is concluded that vacancies can act as strain relievers, thereby reducing their energy of formation. In strained-layer lasers this has the effect of reducing the driving force for DLD growth by climb but increasing the pool of vacancies available for the process to occur. These findings are offered as an explanation for the anomalous behavior of DLDs in strained-layer lasers.

I. INTRODUCTION

Three modes of laser degradation in the quantum well region (i.e., excluding the facets) can be identified, occurring over different time scales. Catastrophic failure or burnup is immediate, intermediate degradation ranges from a few minutes to a few hundred hours of operation, and gradual degradation occurs over thousands of hours of operation. The main mechanism for intermediate degradation is the growth of dark line defects (DLDs), while gradual degradation may be the result of slowly growing DLDs, point-defect clusters, or the formation of dislocation microloops.

The preferred pump wavelength for erbium-doped optical fiber amplifiers is 980 nm, and efficient lasers operating at this wavelength are now commercially available. The active region of these lasers comprises a compressively strained $In_xGa_{1-x}As$ quantum well in a GaAs/AlGaAs heterostructure. The presence of a strained layer raises questions over the reliability of these lasers since the strained layer might seem intuitively to be less stable than an unstrained layer. These concerns have been partially allayed by reports of cw operation of strained-layer lasers for periods of over 18 000 h and the elimination of "freak" failures.[1] However, since telecommunications companies expect a twenty-year (200 000 h) lifetime or longer, the gradual degradation of strained-layer lasers remains a cause for concern.

II. DARK LINE DEFECT (DLD) FORMATION

Transmission electron microscope (TEM) studies[2,3] have revealed that DLDs are three-dimensional dislocation networks, thought to be confined to the quantum well vicinity. They contain elongated dislocation structures, called dipoles, and dislocation loops. DLDs can form within the active region (as defined by the contact stripe) or they can propagate into it. The networks appear to be nucleated by threading dislocations that traverse the multilayer structure. The Burgers vectors of the dislocations are of type $a/2\langle 110\rangle$.

Waters *et al.*[4,5] found that, in unstrained AlGaAs quantum well semiconductor lasers, DLDs grow predominantly in $\langle 100\rangle$ directions, i.e., at 45° to the $\langle 110\rangle$ stripe direction. They observed some growth along $\langle 110\rangle$ directions, but this was much slower. In their strained-layer InGaAs and InAlGaAs quantum well heterostructure lasers, DLD growth along $\langle 100\rangle$ directions was practically eliminated while the much slower growth along $\langle 110\rangle$ still occurred. It is generally accepted that $\langle 100\rangle$ DLDs propagate by dislocation climb and $\langle 110\rangle$ DLDs propagate by dislocation glide.[6] Waters *et al.*[5] suggest that the resistance of the strained layer lasers to $\langle 100\rangle$ DLD propagation might be due to dislocation pinning by indium atoms, as was originally proposed by Kirkby.[7] However, it is unclear why the climb mechanism would be affected but not the glide mechanism.

Since $\langle 100\rangle$ DLDs can cause serious laser degradation, a proper understanding of the climb mechanism is essential. Climb occurs through the diffusion of point defects, for which the activation energy can be supplied by nonradiative recombination of electrons and holes. Such recombinations occur preferentially at dislocations during laser operation since the strain field of the dislocation distorts the electron and hole energy levels.

DLDs have been observed to show an incubation period before propagation begins, and the process has been found to saturate after a period of growth. Growth and saturation have also been observed in TEM by using the electron beam to inject carriers.[8] A possible explanation would be that, initially, there are insufficient sites for climb to occur, so the process is slow. Each climbing portion creates a jog, which encourages further climb, and so the process accelerates. This also helps to explain the ragged dislocation structures that are observed. Eventually the supply of point defects is exhausted and the process stops.

Petroff and Kimerling[8] have produced a detailed model of a possible climb mechanism that relies upon the presence of a large number of point defects. Assuming an excess of Ga interstitials, they show how these would diffuse to a dislocation, thereby causing climb. In so doing, the interstitials are mopped up, and a trail of As vacancies is left behind. The driving force for this process is that Ga interstitials have a lower chemical potential than As vacancies owing to their larger size. However, Barraff and Schluter[9] have shown that the presence of either Ga or As interstitials is energetically unfavorable. Thus, although Petroff and Kimerling considered interstitial diffusion, the current study assumes that

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DLD proceeds through vacancy diffusion. Further support of this assumption can be gathered from the reported TEM observation[6] indicating that the dislocation dipoles within the DLDs are intrinsic, i.e., vacancy type.

III. A VACANCY-CONTROLLED MODEL OF DLD GROWTH

At 800 K, a typical temperature for the growth of specimens by molecular beam epitaxy (MBE), the equilibrium concentration of vacancies is many orders of magnitude higher than at room temperature. However, a specimen held briefly at this temperature would not be expected to reach equilibrium. This can be demonstrated by considering the diffusion distance for vacancies over a 1 h period at 800 K, using the following relationships:

$$D=D_0 \exp(-Q_a/kT), \tag{1}$$

$$x \approx \sqrt{Dt}, \tag{2}$$

where D=the diffusion coefficient for vacancies in GaAs, Q_a=the activation energy for diffusion, x=the diffusion distance, and t=the time. Using values[10] $Q_a=2.72$ eV and $D_0=9.62\times10^{-5}$ $m^2\,s^{-1}$, and putting $T=800$ K, $k=8.6\times10^{-5}$ eV/K and $t=3600s$, yields $x=1.5$ nm.

Thus x is much less than the distance between sources or sinks of vacancies, namely, crystal surfaces or dislocations. Thus, after 1 h at 800 K, the concentration of vacancies could not have reached equilibrium. However, as a structure is grown layer by layer in MBE, it would be expected to adopt the equilibrium vacancy concentration *as it grows.* Since the vacancies are comparatively immobile (demonstrated by the calculation above), a substantial portion of vacancies would be "frozen in" when cooling a specimen after MBE growth, leaving a supersaturation of vacancies.

The equilibrium vacancy concentration C_v expressed as a fraction of the total number of lattice sites is given by

$$C_v \approx \exp(-Q_v/kT), \tag{3}$$

where Q_v is the energy of formation of a vacancy. During operation of a conventional unstrained quantum well laser, some vacancies might become mobile as a result of nonradiative electron-hole recombination. These vacancies can annihilate by migration to a dislocation, causing the latter to climb. This would be observed as DLD growth in $\langle 100\rangle$ directions, and the driving force would be the removal of the supersaturation of vacancies.

In this model, DLD growth occurs by the diffusion of vacancies to existing dislocations. Jogs are formed; these become extended through a climb process as more vacancies arrive. The subsequent extended dislocation structures are the interstitial (vacancy-type) dipoles that characterize DLDs. DLD growth by climb therefore involves vacancy annihilation at the expense of the extension of a dislocation network. For this to be a favored process, the net change in energy ΔQ must be negative. ΔQ is given by

$$\Delta Q=Q_d-Q_v, \tag{4}$$

where

Q_d=energy of extra dislocation length,

Q_v=energy of formation of vacancy.

Thus the energy of formation of a vacancy Q_v is a critical parameter, determining both the viability of DLD growth by climb and the concentration of vacancies available for such a process.

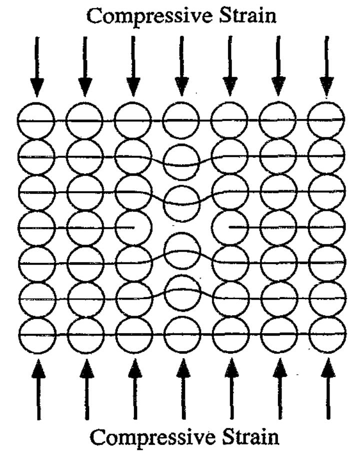

FIG. 1. A vacancy relieving compressive strain.

IV. VACANCIES AS STRAIN RELIEVERS

A vacancy in a compressed $In_xGa_{1-x}As$ layer can relieve some of the strain energy Q_s of the strain field in which it sits, as shown in Fig. 1. This has the effect of reducing the energy of formation of a vacancy Q_v so that the modified energy of formation of a vacancy Q_v' is given by

$$Q_v'=Q_v-Q_s. \tag{5}$$

In fact, Q_v' is reduced still further since Q_v implicitly contains a term expressing the tensile strain energy of a vacancy in an otherwise undistorted lattice. When the vacancy is in a compressive strain field, the components of its own tensile strain field that lie parallel to the applied field are cancelled out. This contribution to the reduction in Q_v' is ignored in the current model, which considers only the reduction brought about by Q_s [Eq. (5)].

The following calculation of Q_s is based on the principle that $In_xGa_{1-x}As$ containing vacancies has a smaller lattice constant than $In_xGa_{1-x}As$ which contains no vacancies. A primitive cell containing a vacancy is therefore treated as though it were a complete primitive cell with a smaller lattice constant. Once the reduced lattice constant is known, the strain energy due to the mismatch to the GaAs layer can be calculated and compared to the strain energy of vacancy-free $In_xGa_{1-x}As$ on GaAs. Throughout the derivation, $In_xGa_{1-x}As+v$ refers to material containing vacancies and $In_xGa_{1-x}As$ refers to vacancy-free material.

It is assumed that vacancies substitute for In and Ga atoms in proportion to their relative concentrations and that Vegard's law applies so that the lattice parameter varies linearly with the concentration of vacancies. It is further assumed that the vacancy concentration is not excessive ($<\sim1\%$) and that the shear modulus G and Poisson's ratio ν are unaffected by the presence of vacancies.

Various lattice constant values d are required: d_{GaAs}, d_{InAs}, and d_v. The last is the notional lattice constant derived for an $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ primitive cell containing a single Ga vacancy. Let $\Delta d_{\mathrm{In}}=d_{\mathrm{InAs}}-d_{\mathrm{GaAs}}$ and $\Delta d_v=d_v-d_{\mathrm{GaAs}}$. Notice that Δd_v is negative. If C_v is the vacancy concentration expressed as a fraction of the total number of lattice sites, then

$$d_{\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}+v}=d_{\mathrm{GaAs}}+x\Delta d_{\mathrm{In}}+C_v\Delta d_v\,. \tag{6}$$

The energy per unit volume arising from a strain ϵ is given by

$$Q_\epsilon=2G\left(\frac{1+\nu}{1-\nu}\right)\epsilon^2. \tag{7}$$

For $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$,

$$\epsilon=\frac{d_{\mathrm{GaAs}}-d_{\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}}}{d_{\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}}}=\frac{-x\Delta d_{\mathrm{In}}}{d_{\mathrm{GaAs}}+x\Delta d_{\mathrm{In}}}, \tag{8}$$

and for $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}+v$,

$$\epsilon=\frac{d_{\mathrm{GaAs}}-d_{\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}+v}}{d_{\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}+v}}=\frac{-x\Delta d_{\mathrm{In}}-C_v\Delta d_v}{d_{\mathrm{GaAs}}+x\Delta d_{\mathrm{In}}+C_v\Delta d_v}. \tag{9}$$

Let the difference in strain energy per unit volume between $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ on GaAs and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}+v$ on GaAs be represented as ΔQ_ϵ. Assuming that $C_v \ll 1$ and $\Delta d_{\mathrm{In}} \ll d_{\mathrm{GaAs}}$, then

$$\Delta Q_\epsilon\approx\left(\frac{1+\nu}{1-\nu}\right)\left(\frac{-4GC_v\Delta d_v x\Delta d_{\mathrm{In}}}{d_{\mathrm{GaAs}}^2}\right). \tag{10}$$

This is the strain energy relieved per unit volume by a vacancy concentration C_v expressed as a fraction of the Ga or As lattice sites. If the number of such lattice sites per unit volume is N, then the strain energy relieved per vacancy Q_s is given by

$$Q_s=\frac{\Delta Q_\epsilon}{C_vN}\approx\left(\frac{1+\nu}{1-\nu}\right)\left(\frac{-4G\Delta d_v x\Delta d_{\mathrm{In}}}{Nd_{\mathrm{GaAs}}^2}\right). \tag{11}$$

The values of all these parameters are well established except for x, which is the controlled variable, and Δd_v. If the atoms around a vacancy were to collapse completely into the space created for them, then d_v would be $0.5\times d_{\mathrm{GaAs}}$, and then Δd_v would be approximately -0.28 nm. This is an upper limit for the magnitude of Δd_v, and it is questionable whether Vegard's law would still apply in such an extreme case. If Vegard's law is assumed to apply, the variation of Q_s with x is as shown in Fig. 2 for different values of Δd_v. The following values for the materials parameters have been used: $G=3.3\times10^{10}$ N m^{-2}; $N=2.2\times10^{28}$ m^{-3}; $\nu=0.3$; $d_{\mathrm{InAs}}=0.60584$ nm; $d_{\mathrm{GaAs}}=0.56533$ nm. If the maximum magnitude for Δd_v is assumed, i.e., -0.28 nm, then the strain energy relieved per vacancy when $x=0.2$ is approximately 0.50 eV per vacancy.

Various values for the energy of formation of a vacancy Q_v have been reported in the literature. According to Kröger[11] $Q_v=2.59$ eV, and so the modified value Q_v' for a strained layer is 2.09 eV.

The smaller value of Q_v' compared to Q_v has the effect of tilting the energy balance Eq. (4) against DLD growth in strained-layer structures. However, at the same time the equilibrium concentration of vacancies C_v' is increased [Eq. (3)]. Thus there are more vacancies available to contribute to dislocation climb, but it is less energetically favorable for them to do so.

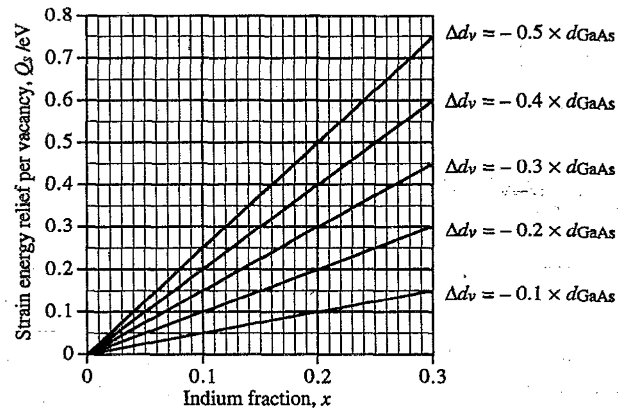

FIG. 2. Strain energy relief per vacancy Q_s as a function of the indium fraction x

V. JOG FORMATION

Calculating the extra dislocation line energy Q_d created by a single migrating vacancy is not straightforward. If the vacancy arrives at a straight dislocation segment [Fig. 3(a)], a simple jog is formed [Fig. 3(b)]; however, vacancies that subsequently extend the width of an existing jog may cause no new line length at all [Fig. 3(c)].

The strain energy per unit length of a dislocation is approximately

$$\frac{Gb^2}{4\pi(1-\nu)}\ln\left(\frac{R}{b}\right), \tag{12}$$

where G is the shear modulus for $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$, b is the magnitude of the dislocation Burgers vector, and R is the cutoff radius for the strain field. Consider a vacancy that creates a new jog where the resultant extra dislocation length is $2b$. Assuming values of $b=0.4$ nm and $R=10$ nm, then the extra dislocation energy is $\sim$10 eV. However, if only one in every N' vacancies that condense at a dislocation causes an increase in the dislocation length, then Q_d per vacancy is, on average, $10/N'$ eV.

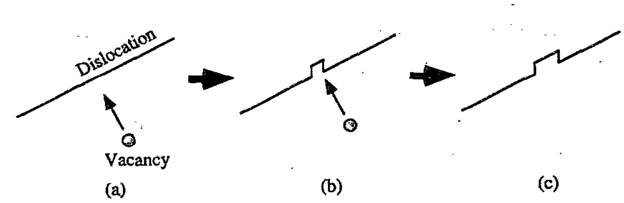

FIG. 3. Jog formation.

VI. DISCUSSION

The calculations shown here are approximate, and the values yielded need to be treated with caution. However, it has been shown that vacancies can act as strain relievers and that their energy of formation in a strained layer is reduced compared to an unstrained structure. This is significant for the climb-controlled growth of ⟨100⟩ dark line defects. The energy balance shown in Eq. (4) determines whether or not DLD propagation by climb takes place. The drop in the energy of formation of a vacancy due to the compressive strain in a layer of $In_{0.2}Ga_{0.8}As$ on GaAs may be as large as 0.5 eV. Such a drop may be sufficient to tilt the energy balance against DLD growth by climb. This effect is offered as a possible explanation of the findings of Waters *et al.*[4,5] that ⟨100⟩ DLD growth was suppressed in their strained layer lasers but not in their unstrained lasers. The glide mechanism that controls ⟨110⟩ growth is unaffected, consistent with their observations.

In the model proposed here, a compressive strain field reduces the energy of formation of vacancies and consequently suppresses DLD growth. The model is based upon the notion that free vacancies relieve compressive strain energy in a strained-layer structure, and that it can therefore be energetically unfavorable for them to diffuse to DLDs. There is an implicit assumption in the model that free vacancies are more effective as strain relievers than the intrinsic (vacancy-type) dislocation dipoles and loops that constitute DLDs. This assumption can be justified on two counts. First, the condensation of vacancies at an intrinsic dislocation dipole or loop is likely to cause localized tension while the surrounding crystal remains in compression. Thus the net strain energy would remain high. Second, the dislocation dipole structures of DLDs are elongated in {100} planes parallel to the layers.[2] Thus they would lie parallel to the strain field in a strained-layer laser and the strain relief would be small.

There are still good reasons to remain cautious about the stability of strained-layer structures. The reduction in the value of Q_v' for strained-layer structures also has the effect of increasing the concentration of vacancies available for the climb process to proceed. If the reduction in Q_v' is inadequate to tilt the energy balance represented in Eq. (4), then the increased number of vacancies may be the dominant effect. At a typical MBE growth temperature of 800 K, a reduction in Q_v' from 2.59 to 2.09 eV would increase the equilibrium vacancy concentration by a factor of more than 1400. Metalorganic chemical vapor deposition (MOCVD) takes place at higher temperatures (typically, at 1100 K) and so the vacancy concentrations in specimens grown this way are likely to be higher still. This effect is partially offset by the greater mobility of vacancies at MOCVD growth temperatures, and the number surviving at room temperature will depend on the rate of cooling.

VII. CONCLUSIONS

A model of DLD growth by vacancy diffusion has been proposed. The model is based upon the assumption that structures grown by MBE or MOCVD contain a high concentration of vacancies, which are rendered mobile by nonradiative electron-hole recombinations during the operation of the laser. In the case of an unstrained structure, the vacancies migrate towards dislocations, causing them to climb. This is observed as DLD growth. In strained-layer lasers, the vacancies act as strain relievers, thus reducing their energy of formation. This reduction may cause the vacancies to remain as isolated point defects rather than contribute to DLD growth. However, the reduction in the energy of formation of vacancies also serves to increase the number of vacancies present. When this effect dominates, DLD propagation could actually be enhanced by the strained layer.

The proposed model is consistent with the observation that dislocation movement by climb in ⟨100⟩ directions is suppressed in strained-layer structures, but the slower glide in ⟨110⟩ is not. Both mechanisms occur in unstrained lasers. It has been reported that electron-beam induced climb in a TEM cannot be maintained indefinitely,[8] consistent with the supply of vacancies being exhausted. The observation that DLD growth is accelerated in lasers operated at temperatures below room temperature[12] is also consistent with the model as there is an even greater supersaturation of vacancies at reduced temperatures. By a similar argument, structures grown by high temperature methods such as MOCVD have higher vacancy concentrations and may therefore be less stable than those grown by lower temperature methods such as MBE.

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