Control of strain in GaN using an In doping-induced hardening effect

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We study the hardening effect by isoelectronic In doping on strain in GaN grown by metalorganic vapor phase epitaxy. Incorporated In into GaN was found to pin the slip of screw dislocations, producing internal resistance stress in GaN as a result of the hardening of GaN. We found that this result is due to the interaction between In atoms and screw dislocations. The calculated stress in GaN yielded by the interaction was found to be in good agreement with the measured stress by x-ray diffraction and Raman spectroscopy. The internal resistance stress was estimated to be 0.3 GPa at maximum.

I. INTRODUCTION

The use of a low-temperature deposited buffer layer in the growth of GaN on sapphire enables us to grow high-quality films without cracks,[1] although there are high-density threading dislocations on the order of 10^8–10^{11} cm^{-2}. Recently, the reduction of threading dislocations has been achieved by epitaxial lateral overgrowth[2] or the low-temperature interlayer technique.[3,4] We have attempted to use other approache to reduce defects, that is, isoelectronic In doping. Several effects of strain associated with isoelectronic impurity doping on the crystalline quality was observed. The In doping into GaN has been recently reported by some research groups,[5,6] together with its effect on crystalline quality and optical properties. We have recently investigated the effect of In doping on controlling the strain in GaN,[6,7] and found that this technique is also useful for the improvement of crystalline and optical properties of quantum wells.[8,9] In this paper, the controllability of strain in GaN by isoelectronic In doping and its mechanism in terms of the interaction between In and screw dislocations are discussed.

II. EXPERIMENT

All undoped and In-doped GaN samples studied here were grown by metalorganic vapor-phase epitaxy at 1000 °C in H_2 or N_2 carrier gas (denoted below by H_2-GaN and N_2-GaN, respectively). In was doped into GaN by supplying trimethylindium (TMI) during the growth of the GaN layer. The thickness of GaN was set at 2.7 μm. Lattice constant c was determined by the conventional (0002) $2\theta/\omega$-scan x-ray diffraction measurement, and lattice constant a was determined directly using $(10\bar{1}0)$ $2\theta/\omega$-scan grazing incident x-ray diffraction measurement. In concentration in some GaN samples was measured by secondary-ion mass spectroscopy (SIMS).

III. RESULTS AND DISCUSSION

Figure 1 shows the relationship between the strain of lattice constant c and that of lattice constant a o fH_2-GaN (closed circles) and N_2-GaN (open circles). The dashed line was obtained by best fitting the experimental data. The fitted c_0 and a_0 were obtained using the theoretical expression,[10] $\Delta c/c_0 = -2(C_{13}/C_{33})(\Delta a/a_0)$. C_{13} and C_{33} are the elastic stiffness coefficients for bulk GaN. c_0, a_0 and C_{13}/C_{33} are 5.18497 Å, 3.18874 Å and 0.21288 Å, respectively, which are very close to the data reported for bulk GaN.[11] The direction of the arrows indicates the direction of increase in In concentration in GaN. H_2-GaN is under compressive stress and N_2-GaN is under tensile stress at room temperature. With increasing In concentration, lattice constants c and a of both H_2-GaN and N_2-GaN approached the values for bulk GaN. It should be noted that GaN grown with low-temperature deposited buffer layer is under tensile stress at growth temperature.[12]
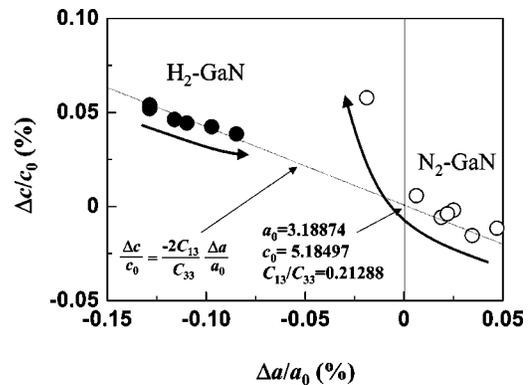

FIG. 1. $\Delta c/c_0$ as a function of $\Delta a/a_0$. (H_2-GaN with thickness of 2.7μm (closed circles). N_2-Ga with thickness of 2.7μm (open circles)). The dashed line denotes the relationship between $\Delta c/c_0$ and $\Delta a/a_0$ estimated by calculation. The direction of the arrows indicates that of the increase in In concentration in GaN.
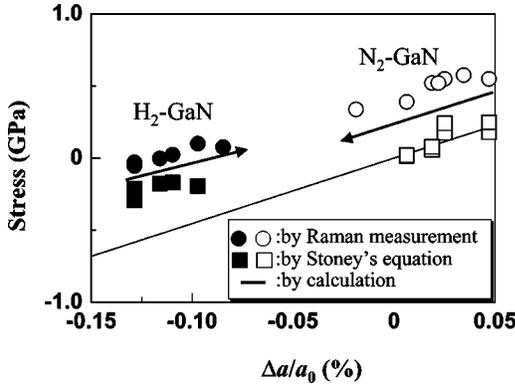
FIG. 2. Biaxial stress in GaN obtained by Raman measurement as a function of $\Delta a/a_0$ (closed and open circles). Biaxial stress in GaN obtained by Stoney's equation as a function of $\Delta a/a_0$ (closed and open squares). The relationship between strain and stress in bulk GaN according to Eq. (3) (solid line).

In Fig. 1 the plots of $\Delta c/c_0$ as a function of $\Delta a/a_0$ lie along the theoretical line for almost the entire range of In concentration. In general, for $Ga_{1-x}In_xN$ alloy, lattice constants a and c characterizing the hcp (Ga, In) sublattice increase approximately linearly with In concentration. We consider that in the concentration range of In in GaN less than 1×10^{20} cm^{-3}, In acts as a strain absorber, so that the total energy be reduced further. However, for a larger In concentration ($>1 \times 10^{20}$ cm^{-3}), the plot of $\Delta c/c_0$ as a function of $\Delta a/a_0$ deviates from the theoretical line, implying the beginning of the formation of $Ga_{1-x}In_xN$. Consequently, In in some concentration region serves mainly to relieve the strain in GaN, and for a larger In concentration region, it serves mainly to form $Ga_{1-x}In_xN$.

Figure 2 shows biaxial stress in GaN obtained by three different measurements; (i) Raman shift of the $E2$ mode as a function of $\Delta a/a_0$ (closed and open circles for H$_2$- and N$_2$-GaN, respectively), (ii) Stoney's equation as a function of $\Delta a/a_0$ (closed and open squares H$_2$- and N$_2$-GaN, respectively), (iii) theoretical calculation using a set of C_{ij} ($i,j = 1,2,3,4$) (solid line) as follows.

Biaxial stress σ_a in GaN obtained using Raman shift was also derived from the following equation.[14]

$$\Delta\omega_{E_2} = \sigma_a \times 4.2 \text{cm}^{-1}/\text{GPa}, \qquad (1)$$

where the E2 line of bulk GaN (Ref. 11) was set at 568 cm^{-1}. Biaxial stress in GaN obtained using Stoney's equation was derived from the following equation.[15]

$$\sigma_a = \frac{(E_s t_s^3 + E_g t_g^3)\kappa}{6(1-\nu_s)(t_s+t_g)t_g}, \qquad (2)$$

where E is Young's modulus, t is thickness, ν is Poisson's ratio, and κ is the curvature of GaN. The suffixes, s and g, mean substrate and GaN, respectively. As those constants, we used the following values, biaxial modulus $M_s \equiv E_s/(1-\nu_s) = 602$ GPa,[12] $E_g = 346$ GPa $= M_g \times (1-\nu_g)$, where
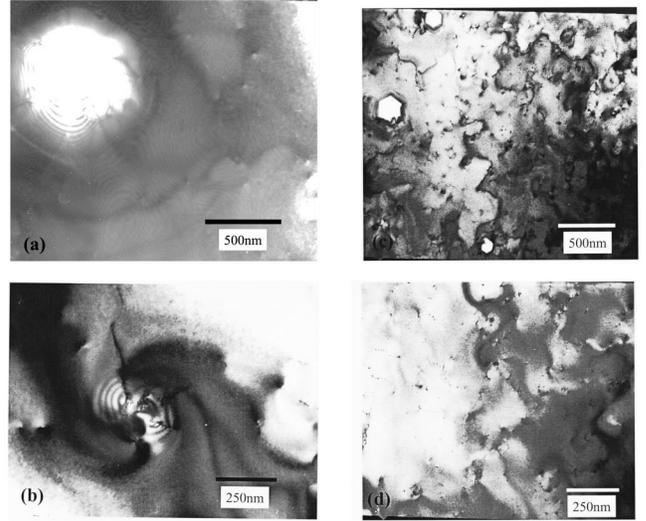

FIG. 3. TEM images. (a) plan view of H$_2$-GaN without In doping, (b) plan view of H$_2$-GaN with In doping, (c) plan view of N$_2$-GaN without In doping, and (d) plan view of N$_2$-GaN with In doping.

$\nu_g = 0.23$,[12,14] $t_s = 330$ μm, and $t_g = 2.7$ μm. As κ experimental results obtained by wafer curvature measurement were used.

On the other hand, biaxial stress in GaN can be obtained using the following expression.[16]

$$\sigma_a = \left(C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}}\right)\frac{\Delta a}{a_0}. \qquad (3)$$

The elastic constants, $C_{11} = 374$ GPa, $C_{12} = 106$ GPa, $C_{44} = 101$ GPa, $C_{33} = 379$ GPa, and $C_{13} = 70$ GPa are adopted[11] for our samples because the value of C_{13}/C_{33} was closest to that when using one set of those constants. Using those values, we plotted Eq. (3) in Fig. 2.

The values obtained by the above three ways are seen to be in fairly good agreement, meaning that In doping definitely produces σ_a according to the deformation of bulk GaN.

As shown above, In doping has been found to control the strain in GaN; moreover, it improved the crystalline quality and the surface structure.[6,7]

Figures 3(a) and 3(b) show bright-field plan view TEM images of H$_2$-GaN obtained with diffraction vector **g** $= [000\bar{2}]$ with or without In doping, respectively. In Fig. 3(a), a growth pit associated with screw dislocations is seen in H$_2$-GaN, while for the sample with In doping, no pit is seen. In Fig. 3(b), screw dislocations are observed to pin those dislocations. Similar results are seen for N$_2$-GaN samples as shown in Figs. 3(c) and 3(d). In fact, cross-sectional TEM observation revealed as below that the density of screw dislocations was decreased by In doping while that of edge dislocations was almost unchanged. This means that In atoms suppress the generation and/or accumulaton of screw dislocations rather than that of edge dislocations.
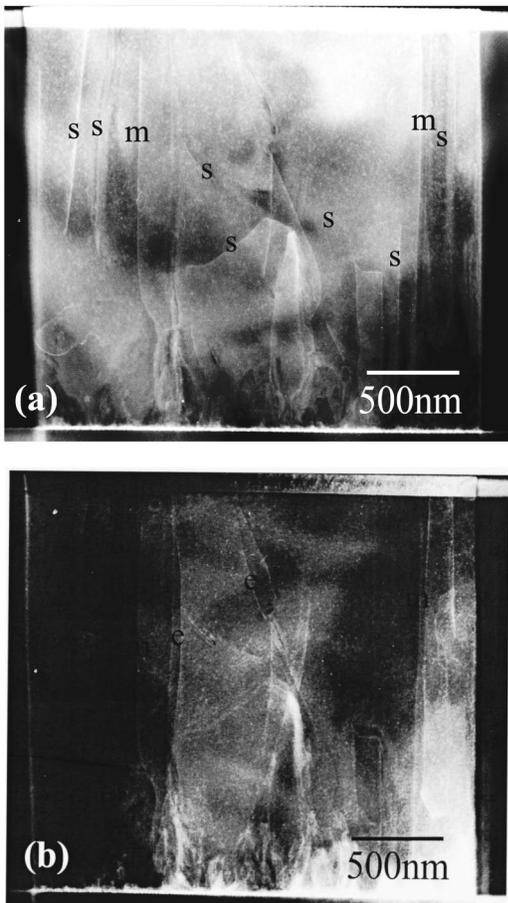
FIG. 4. H_2-GaN without In doping: (a) Cross−sectional view taken with diffraction $g=[000\bar{2}]$. (b) Cross−sectional view taken with diffraction $g=[1\bar{1}00]$.

FIG. 5. H_2-GaN with In doping: (a) Cross−sectional view taken with diffraction $g=[000\bar{2}]$. (b) Cross−sectional view taken with diffraction $g=[1\bar{1}00]$.

Figures 4(a) and 4(b) show cross-sectional view taken with diffraction $g=[000\bar{2}]$ and $g=[1\bar{1}00]$, respectively, for H_2-GaN without In doping. Figure 5(a) and 5(b) show cross-sectional view taken with diffraction $g=[000\bar{2}]$ and $g=[1\bar{1}00]$, respectively, for H_2-GaN with In doping.

From the degree of visibility of the dislocation in the TEM images, we determined the type of dislocation using the relation $\mathbf{g}\cdot\mathbf{b}$, where $\mathbf{g}$ is the diffraction vector and $\mathbf{b}$ is Burgers vector of the dislocation. The marks of ''e,'' ''s'' and ''m'' means edge dislocation, screw dislocation and mixed dislocation, respectively. The pure or mixed screw threading dislocations (TD's) act as centers for spiral growth of GaN by making surface steps, whereas the edge TD's form small angle boundaries of GaN grains slightly misoriented with each other. It has been reported that the threading dislocations which have screw component burgers vectors, have a strong influence on radiative efficiency.[13] The screw and mixed dislocations should act as the dominant nonradiative centers in GaN. In fact, in the samples discussed here, strong enhancement of photoluminescence intensity was observed. For H_2-GaN (N_2-GaN) with In doping, the intensity became 10 (40) times larger than that without In doping.

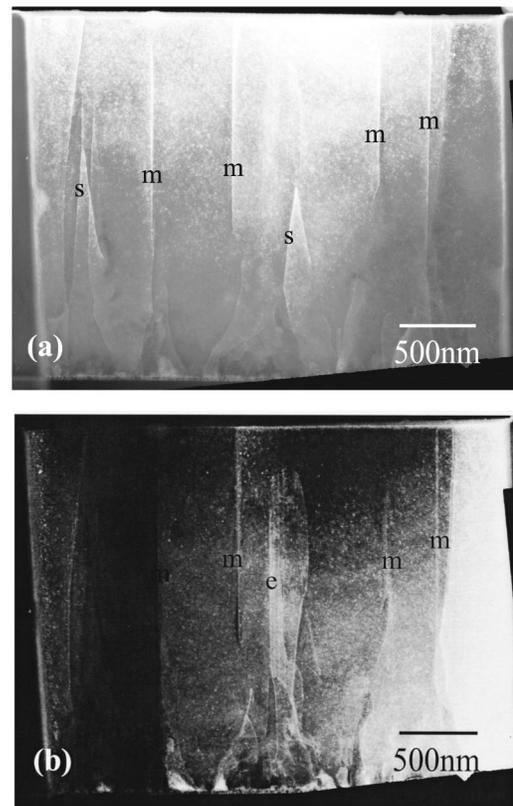Figures 4 and 5 show that with In doping, the density of screw dislocation was reduced. Consequently, the reduction in the density of screw dislocations play an essential role in the mechanism of the decrease in strain in GaN.

Next we discuss the mechanism of strain relief by In doping in terms of interaction between In and screw dislocations. The mechanical properties of a crystal are significantly influenced by the concentration and species of solute atoms contained in it. This is because solute atoms generally affect the motion of dislocations.[17] This influence may inhibit the motion of dislocations and the response of the material against mechanical stress. GaN is plastically deformed mainly during growth and partly during cooling down, and dislocations are introduced in it. In this case, screw dislocations play a significant role in yielding stress, because the extension of dislocations requires cross slip which is characterstic for screw dislocations.[18]

Since a solute atom is generally characterized by a dissimilar size in solid solution from a matrix atom, the solute behaves like an elastic inclusion and gives rise to an elastic strain field. This strain field, in turn, interacts with the stress field of a dislocation, resulting in a solute atom-dislocation misfit interaction. In effect, the interaction arises because the elastic strain energy of a solid containing solute atoms and dislocations is decreased when a solute atom migrates from a position of misfit in the matrix to a position of better accomodation in the region of imperfect packing surrounding a dislocation.

Usually, the solute atom-dislocation interaction is analyzed in terms of linear isotropic elasticity. Of course, GaN is of wurtzite type, but it can be treated in terms of mechanical deformation as an isotropic material using the Voigt approximation,[19] and the validity of such approximation was verified.[14]

In general, the elastic interaction energy between solutes and screw dislocations is important, and an approach to calculate the interaction with screw dilocations is considered. The interaction energy[19] is obtained by Eq. (4), as

$$U_e^s = \frac{2K\epsilon\mu(1+\nu)r_0^3}{3\pi(1-2\nu)}\frac{b^2}{r^2}, \tag{4}$$

where μ is the shear modulus, ν is Poisson's ratio, $\epsilon = (r_s - r_m)/r_m$ is the ratio of sizes of Ga and In, and $b = 5.185$ Å is the magnitude of Burger's vector for the screw dislocation in this case. r_0 is the bond length of Ga-N, and is 1.94 Å.

In addition, there is a contribution to the interaction whenever the solute and the solvent possess dis-similar elastic moduli, since the solute atom behaves as an elastic inhomogeneity in the dislocation strain field. According to the linear-elasticity theory, these two interactions (misfit and modulus) can be treated independently. The expression for the energy of interaction between solute atoms of a different modulus from the matrix and screw dislocations is given by[20,21]

$$U_m^s = \frac{\mu\epsilon_\mu' b^2 r_0^3}{6\pi r^2}, \tag{5}$$

$$\epsilon_\mu' = \frac{1}{\mu}\frac{d\mu}{dx}\left(1+\frac{1}{2\mu}\left|\frac{d\mu}{dx}\right|\right)^{-1}, \tag{6}$$

where x is the molar fraction of In in GaN.

Using Eqs. (4)–(6), the interaction force between a solute and a dislocation is obtained as follows.

$$F_{screw} = -\frac{\partial U_e^s}{\partial X} - \frac{\partial U_m^s}{\partial X} = \frac{\mu b^2 r_0^2}{3\pi r^4}|\epsilon_\mu' + \alpha\epsilon|, \tag{7}$$

where ϵ_μ' is related to elastic modulus and concentration of solutes,

$$\text{and}\quad \alpha = \frac{4K(1+\nu)}{(1-2\nu)},$$

$\epsilon = 0.161$, $r_s = 0.144$ for In and $r_m = 0.124$ for Ga in a tetrahedral structure,[22], and X is the direction normal to the YZ slip plane of screw dislocations. K is unknown, and is treated as a parameter below.

In order to apply this expression to the present data for GaN, we assume isotropic elastic deformation of GaN, and istropic elasticity is assumed with the Voigt approximation.[19] Thus, we use the following relations based on such approximation,

$$\mu = \frac{1}{30}(7C_{11} - 5C_{12} + 2C_{33} + 12C_{44} - 4C_{13}), \tag{8}$$

$$\lambda = \frac{1}{15}(C_{11} + C_{33} + 5C_{12} + 8C_{13} - 4C_{44}), \tag{9}$$

$$\nu = \frac{\lambda}{2(\mu+\lambda)}. \tag{10}$$

We obtained $\mu = 126$ GPa, $\lambda = 96$ GPa, and $\nu = 0.22$. To get values using Eq. (7), the value of ϵ_μ' is necessary; thus we estimate it assuming that the shear modulus linearly changes with In molar fraction, and obtain 0.068 as ϵ_μ'.

The maximum interaction force is given by $F \sim F_{screw}|_{r\sim b}$ at $\theta = \pi/2$ using the Peach-Köhler equation,[23] where θ is the angle between the slip plane and the radial vector. This is the pinning force that the applied stress must overcome in order to move a dislocation. In the force balance condition, F is associated with the dislocation line tension, $T = \mu b^2/2$. The critical bow-out angle of ϕ_c is related to

$$F = 2T\cos\left(\frac{\phi_c}{2}\right). \tag{11}$$

The force due to the applied stress on the slip plane that balances the line tension is σbL, where L is the average spacing between In atoms. The critical stress $\sigma_c bL$ is such that

$$F = \sigma_c bL. \tag{12}$$

For example, using Eq. (11), $F = 2T\cos\phi/2 = \mu b^2\cos\phi/2$, and we obtain $\phi_c/2 = 87.8°$ when In concentration is 1×10^{19} cm^{-3}, and then, the spacing between solute atoms is $L = 9b$. Through such an analysis procedure, we obtain $F \sim (\mu b^2/3\pi)(x/r)|\epsilon_\mu' + \alpha\epsilon| = 0.6994|\epsilon_\mu' + \alpha\epsilon|b^2$, where $x/r = \sin\theta \sim 1$. Moreover, using the expression $F = \sigma_c bL$, we obtain $\sigma_c = F/mb^2$, where $L = mb$. Here, m is the number of averaged spacing of solutes. Thus, we plotted values of σ_c as a function of In concentration in Fig. 6 (solid and dashed lines). Although K is unknown, the calculated values are in best agreement with experimental values in Fig. 6 for $K = 0.4$ (solid line), a value that is close to the value reported for metallic alloys.[20]

Here we define the internal resistance stress σ_{int} as σ_a-σ_0, where σ_a is the measured stress for each sample and σ_0 is the measured stress for the sample without In doping. We consider that σ_{int} results from the stress yielded in GaN against external stress. We plot it in Fig. 6 for H$_2$-GaN (closed circles) and N$_2$-GaN (open triangles) as a function of In concentration in GaN (we confirmed that In concentration was proportional to TMI flow rate for the samples measured by SIMS).

It is found that in Fig. 6 the data for the internal resistance stress and calculated stress based on the interaction between In atoms and dislocations are in good agreement. This suggests that the phenomenon is a result of the interaction between screw dislocations and In atoms. In concentration at the maximum stress (5×10^{20} cm^{-3}) corresponds to $\sim 1\%$

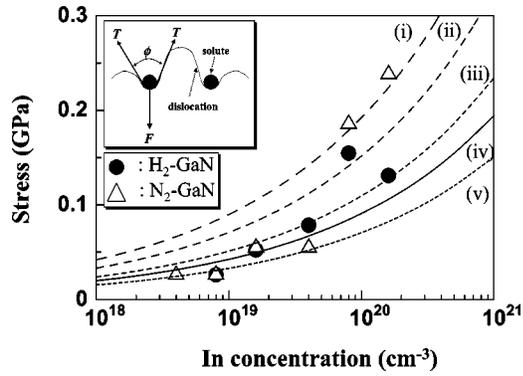FIG. 6. Internal resistance stress $|\sigma_a - \sigma_0|$ as a function of In concentration (closed and open circles). Calculated values of σ_a based on the interaction between In atoms and dislocations as a function of concentration of In (solid and dashed lines), where K = (i) 0.9, (ii) 0.7, (iii) 0.5, (iv) 0.4, (v) 0.3. The inset shows a model explaining the interaction between In atoms and screw dislocations.

In atoms in GaN. It should be noted that In concentration over 1×10^{20} cm^{-3}, the data points get deviated from the line at $K = 0$, implying that the role of In atoms becomes different from that of those for In concentration less than 1×10^{20} cm^{-3}. This supports that the fact that around 1×10^{20} cm^{-3} Ga$_{1-x}$In$_x$N mixed crystals begin to form as shown in Fig. 1.

When the data of resistance stress in Fig. 6 are fitted to $\sigma_{int} \propto x^n$, we obtain the values of n being 0.57 and 0.64 for H$_2$-GaN and N$_2$-GaN, respectively. Here, C being In cocentration, it can be related to[20] $2b^2/L^2 \phi / \sim C^{2/3}$, which, using Eqs. (11) and (12), is reduced to[20] $\sigma_{int} \propto x^n$ ($0.5 \leqslant n \leqslant 1$), where x is the molar fraction of In in GaN and σ_{int} is the force needed to move a dislocation at $T = 0$ K. Although this fact may not be related directly to experimental data in Fig. 6, it will support the results shown in Fig. 6.

IV. CONCLUSION

We studied the mechanisms of change of strain in GaN using isoelectronic In doping. Incorporated In solute atoms in GaN were found to pin mainly the slip of screw dislocations, and this led to the hardening of GaN, resulting in the production of internal resistance stress in GaN.

ACKNOWLEDGMENTS

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