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Biaxial Relaxation Coefficient in Group-III Nitride Quantum Wells and Thin Films

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We apply the third-order elasticity theory to study the biaxial relaxation coefficient (the R_B coefficient) in group-III nitride quantum wells and thin films. The R_B coefficient determines the ratio between the out-of-plane and in-plane strain components in these strained layers. We show that the R_B coefficient in four material systems, i.e., AlN thin films grown on $Al_xGa_{1-x}N$ substrates, GaN quantum wells grown on $Al_xGa_{1-x}N$ substrates, GaN thin films grown on $In_xGa_{1-x}N$ virtual substrates, and InN quantum wells grown on $In_xGa_{1-x}N$ virtual substrates, to a large extent, depends on the in-plane strain arising from the lattice misfit between the strained layers and the substrates. This phenomenon cannot be described by the linear theory of elasticity. We also find that the R_B coefficient in most of the quantum wells and thin films made of $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$ alloys significantly depends on the in-plane strain, which is reflected by the observed discrepancies between the results obtained using third-order elasticity and linear elasticity. These discrepancies are proportional to the magnitude of the in-plane strain for $Al_xGa_{1-x}N$ thin films and $In_xGa_{1-x}N$ quantum wells grown on GaN substrates and they vanish when Al or In contents are smaller than 0.2. For $Al_xGa_{1-x}N$ the quantum wells grown on AlN substrates and $In_xGa_{1-x}N$ thin films grown on InN substrates, we find that the discrepancies between the results obtained using third-order elasticity and linear elasticity are not proportional to the in-plane strain. Unusual behaviour of the R_B coefficient in group-III nitride alloys originates from the different values of the elastic constants for the binary nitride semiconductors, causing the opposite dependences of the R_B coefficient on strain for GaN compared to InN and AlN.

topics: third-order elasticity, biaxial relaxation coefficient, group-III nitrides, thin films

1. Introduction

A common feature of nanostructures built from group-III nitride semiconductors is the presence of strains, which originate from large differences in lattice parameters and thermal expansion coefficients between nitride materials [1]. Strain changes the energy bands of semiconductor structures, altering their fundamental physical properties, such as the energy gap and the energy of the optical transitions [2, 3]. In thin films (TFs) and quantum wells (QWs) grown on *c*-plane substrates, internal biaxial stress in a plane perpendicular to the *c*-axis of the wurtzite lattice generates a biaxial strain, which is described by in-plane and out-of-plane strain components [4]. Both these strain components are related to each other via a single parameter, called the biaxial relaxation coefficient R_B [5]. For many years this coefficient was studied experimentally and theoretically, assuming that it is a strain-independent quantity [4–16]. Theoretical estimations of the R_B coefficient were obtained on the basis of first-principles calculations of the second-order elastic constants (SOECs) and the application of the linear theory of elasticity, which predicts that it is equal to $2C_{13}/C_{33}$ [4–10]. The experimental investigations of the R_B coefficient were focused on measurements of strain in TFs using high-resolution X-ray diffraction and transmission electron microscopy [11–13]. The results of these measurements were also interpreted assuming no strain dependence of the R_B coefficient, in accordance with the linear theory of elasticity.

Recently, we have revealed by the hybrid-density functional theory calculations that the R_B coefficient depends significantly on strain in the group-III nitride semiconductors [14]. In particular, we have shown that for InN and AlN, the R_B coefficient increases significantly with the in-plane strain, while it decreases in GaN. This effect is well-described by the third-order elasticity theory [14]. In the present work, we study the R_B coefficient in concrete group-III nitride QWs and TFs, which can be easily obtained experimentally and are commonly used in electronic and optoelectronic devices. We show that for the majority of nitride strained layers,

TABLE I

The lattice constants (in [Å]) and the elastic constants (in [GPa]) for the group-III nitrides in wurtzite symmetry.

	a	c	C_{13}	C_{33}	C_{113}	C_{123}	C_{133}	C_{333}
AlN	3.103^a	4.970^a	111.1^b	387.4^b	-248^b	-465^b	-1097^b	-1024^b
	3.112^c	4.982^c	98.9^d	388.5^d				
GaN	3.180^a	5.172^a	95.7^b	406.3^b	-368^b	-458^b	-937^b	-2341^b
	3.189^c	5.185^c	106^e, 97.5^f	398^e, 398.1^f				
InN	3.542^a	5.711^a	91.9^b	238.4^b	-399^b	-479^b	-762^b	-860^b
	3.545^c	5.703^c	108^g	265^g				

Theoretical: [a]Ref. [15], [b]Ref. [14]; experimental: [c]Ref. [16], [d]Ref. [17], [e]Ref. [18], [f]Ref. [19], [g]Ref. [20]

the results obtained using the third-order elasticity theory differ significantly from those predicted by the linear theory of elasticity, which neglects the influence of strain on the R_B coefficient.

2. The model of the R_B coefficient

Within the framework of the third-order elasticity theory, for QWs and TFs grown along the c axis of the wurtzite lattice, the R_B coefficient is given by

$$R_B = \frac{1}{\varepsilon_{xx}}\left[1-\sqrt{1+\frac{2}{C_{333}}\left(-c+\sqrt{c^2-2C_{333}d}\right)}\right], \tag{1}$$

where $c = C_{33} + 2C_{133}(\varepsilon_{xx} + \frac{1}{2}\varepsilon_{xx}^2)$ and $d = 2C_{13}(\varepsilon_{xx} + \frac{1}{2}\varepsilon_{xx}^2) + (C_{113} + C_{123})(\varepsilon_{xx} + \frac{1}{2}\varepsilon_{xx}^2)^2$ [14]. In the above formulas, C_{13} and C_{33} are the SOECs, while C_{113}, C_{123}, C_{133}, and C_{333} are the third-order elastic constants (TOECs). The SOECs and the TOECs are defined, respectively, as

$$C_{ij} = \rho_0 \frac{\partial^2 E}{\partial\eta_i \partial\eta_j}, \tag{2}$$

and

$$C_{ijk} = \rho_0 \frac{\partial^3 E}{\partial\eta_i \partial\eta_j \partial\eta_k}, \tag{3}$$

where E is the Helmholtz free energy per unit mass, ρ_0 is the mass density of the unstrained material, and η_i is the Lagrangian strain (in the Voigt notation) [14]. The in-plane strain is determined by the well-known formula $\varepsilon_{xx} = \frac{a_s}{a_l} - 1$, where a_s and a_l are the lattice constants of the substrate and the material of a QW or a TF, respectively. We would like to notice that the R_B coefficient model presented applies to QWs and TFs grown on c-plane substrates, because in both cases we deal with a biaxial strain arising from the lattice misfit between the strained layer and the substrate. In Table I, we present the values of the elastic constants and the lattice parameters obtained for group-III nitrides using the hybrid-density functional theory calculations [14, 15]. The SOECs and TOECs were calculated using the strain-energy method (i.e., with (2) and (3)) combined with an approach based on exact deformation-gradient tensors [14, 21].

For QWs and TFs made of ternary nitride alloys, such as $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$, we take into account the nonlinear composition dependences of the SOECs,

$$C_{ij}\,(M_xGa_{1-x}N) = x\,C_{ij}\,(MN) + (1-x)\,C_{ij}\,(GaN) - b_{ij}\,x\,(1-x)\,, \tag{4}$$

where $C_{ij}\,(MN)$ and $C_{ij}\,(GaN)$ are the SOECs of the binary nitrides (here (MN) denotes (AlN) or (InN)) and b_{ij} are the bowing parameters that account for the deviation of the SOECs from the linear (Vegard-like) dependences on composition [22]. According to the *ab-initio* data presented in [22], we apply $b_{13} = -13.6$ and $b_{33} = 94$ for $In_xGa_{1-x}N$, and $b_{13} = 6.5$ and $b_{33} = -35.9$ for $Al_xGa_{1-x}N$ (unit is [GPa]). We assume that the lattice parameters in nitride alloys depend linearly on composition, which is in good agreement with the results of the *ab-initio* calculations [23]. Since the composition dependences of the TOECs are unknown for the group-III nitride alloys, we use the Vegard-like (linear) approximation for the TOECs.

3. The results and discussion

First, we investigate the R_B coefficient in AlN TFs grown on $Al_xGa_{1-x}N$ substrates. In Fig. 1, we show that the R_B coefficient for AlN TFs (solid line) decreases significantly from 0.613 to 0.574 with increasing Al content x in $Al_xGa_{1-x}N$ substrates. This effect originates from tensile strain in AlN TFs, arising from the lattice misfit between the substrates and the TFs. The linear theory of elasticity predicts no dependence of the R_B coefficient on strain and thus, according to this theory, the R_B coefficient in AlN TFs (dashed line) does not change with the composition of $Al_xGa_{1-x}N$ substrates. The linear theory of elasticity gives the correct value of the R_B coefficient only for infinitesimally small strain, i.e., when the composition of the substrate is very close to AlN. In such a case, we obtain $R_B = 0.574$, which is relatively well in line with the experimental value of the $R_B = 0.556 \pm 0.021$, obtained in [13].

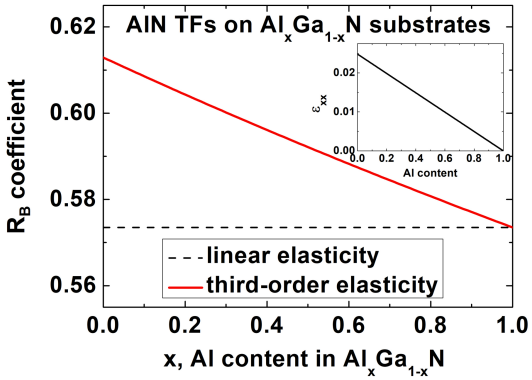

Fig. 1. The R_B coefficient for AlN TFs as a function of Al content in $Al_xGa_{1-x}N$ substrates. Solid (dashed) line corresponds to the results obtained using third-order (linear) elasticity. The inset shows the in-plane strain ε_{xx} as a function of Al content in $Al_xGa_{1-x}N$ substrates.

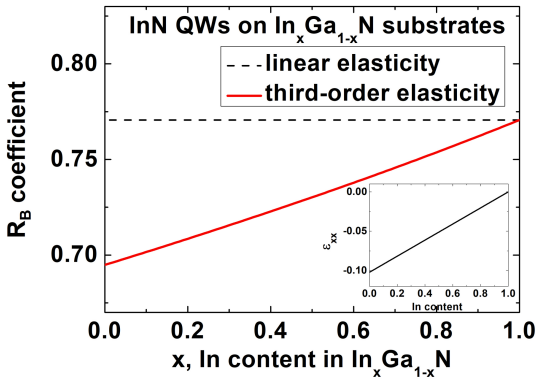

Fig. 3. The R_B coefficient for InN QWs as a function of In content in $In_xGa_{1-x}N$ substrates. Solid (dashed) line corresponds to the results obtained using third-order (linear) elasticity. The inset shows the in-plane strain ε_{xx} as a function of In content in $In_xGa_{1-x}N$ substrates.

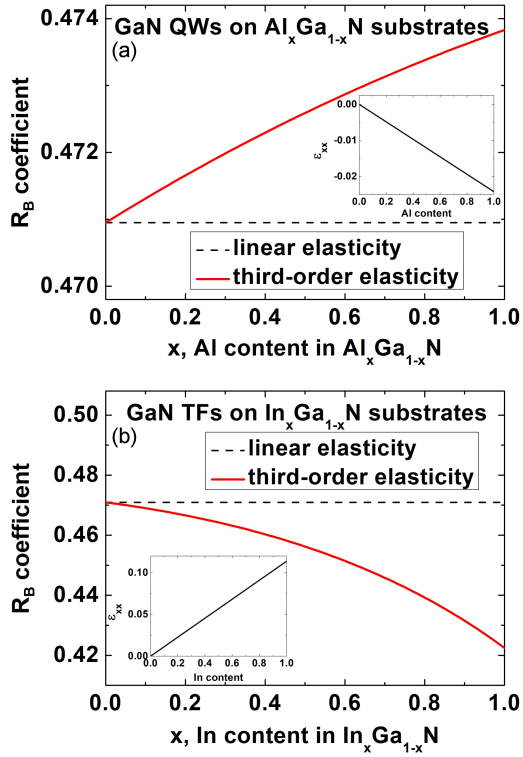

Fig. 2. The R_B coefficient for (a) GaN QWs grown on $Al_xGa_{1-x}N$ substrates and (b) GaN TFs grown on $In_xGa_{1-x}N$ substrates as a function of chemical composition of substrates. Solid (dashed) lines correspond to the results obtained using third-order (linear) elasticity. The insets show the in-plane strain ε_{xx} as a function of chemical composition of substrates.

Then we study the R_B coefficient in GaN strained layers. In Fig. 2, we present the R_B coefficient for GaN QWs grown on $Al_xGa_{1-x}N$ substrates and for GaN TFs grown on $In_xGa_{1-x}N$ virtual substrates, which are represented by fully relaxed $In_xGa_{1-x}N$ thick buffer layers. In the first case, the R_B coefficient of GaN QWs slightly increases from 0.471 to 0.474 with increasing Al content in $Al_xGa_{1-x}N$ substrate. This effect arises from compressive strain in GaN layers. In the second case, we find that due to tensile strain, the R_B coefficient of GaN TFs decreases significantly from 0.471 to 0.422 with increasing In content in $In_xGa_{1-x}N$ virtual substrate. Again, the linear theory elasticity gives the correct value of the R_B coefficient only for GaN layers at infinitesimally small strain, i.e., when the composition of substrate is very close to that of GaN.

Next, we consider InN QWs grown on $In_xGa_{1-x}N$ virtual substrates. In Fig. 3 we observe that due to compressive strain, the R_B coefficient in InN QWs increases significantly from 0.695 to 0.771 with increasing the In content in $In_xGa_{1-x}N$ substrate. As before, the linear theory of elasticity gives the correct value of the R_B coefficient only for InN layers at infinitesimally small strain. In such a case, we obtain $R_B = 0.771$, which is largely inconsistent with the experimental value of $R_B = 0.43 \pm 0.04$, found in [11]. Further studies are needed to resolve this problem.

Figures 1–3 show that the differences between the R_B coefficient calculated using linear elasticity and third-order elasticity are proportional to the amplitude of ε_{xx} and that is why they are greatest when the strained layers and the substrates are made from different binary nitride compounds. In Table II, for these extreme cases, we present the values of the R_B coefficient, the out-of-plane strain component ε_{zz} and the c lattice parameter obtained using linear elasticity and third-order elasticity. The significant differences between the results obtained using these two approaches underline the importance of applying the third-order elasticity theory in the analysis of the strain effects in nitride heterostructures.

TABLE II

The values of ε_{xx}, the R_B coefficient, the out-of-plane strain component ε_{zz}, and the c lattice parameter (in [Å]), obtained using linear elasticity and third-order (nonlinear) elasticity for A/B heterostructures made from different binary nitride compounds, where A and B denotes a strained layer and a substrate, respectively.

A/B	ε_{xx}	R_B^{linear}	$R_B^{\text{nonlinear}}$	$\varepsilon_{zz}^{\text{linear}}$	$\varepsilon_{zz}^{\text{nonlinear}}$	c^{linear}	$c^{\text{nonlinear}}$
AlN/GaN	0.02482	0.57351	0.61291	−0.01423	−0.01521	4.89927	4.89441
GaN/AlN	−0.02421	0.47095	0.47383	0.01140	0.01147	5.23098	5.23134
GaN/InN	0.11384	0.47095	0.42247	−0.05361	−0.04809	4.89472	4.92327
InN/GaN	−0.10220	0.77065	0.69484	0.07876	0.07101	6.16081	6.11656

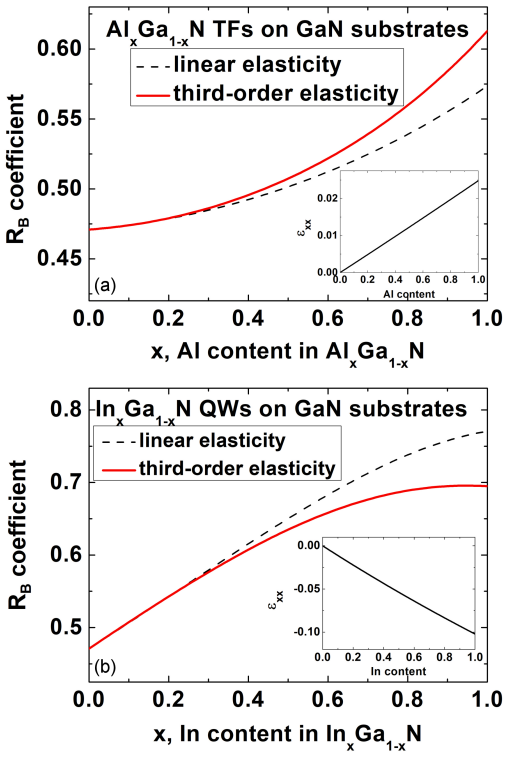

Fig. 4. The R_B coefficient for (a) $Al_xGa_{1-x}N$ TFs and (b) $In_xGa_{1-x}N$ QWs grown on GaN substrates as a function of chemical composition of the strained layers. Solid (dashed) lines correspond to the results obtained using third-order (linear) elasticity. The insets show ε_{xx} as a function of chemical composition of strained layers.

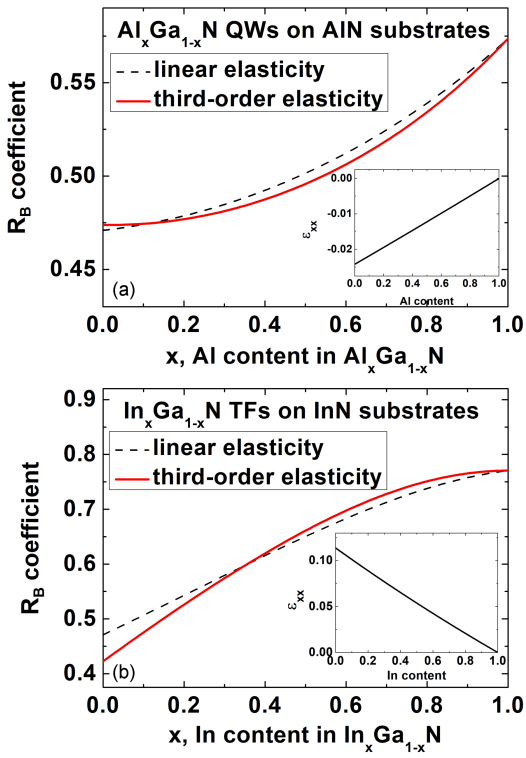

Fig. 5. The R_B coefficient for (a) $Al_xGa_{1-x}N$ QWs grown on AlN substrates and (b) $In_xGa_{1-x}N$ TFs grown on InN substrates (b) as a function of chemical composition of the strained layers. Solid (dashed) lines correspond to the results obtained using third-order (linear) elasticity. The insets show ε_{xx} as a function of chemical composition of strained layers.

Finally, we study the R_B coefficient in QWs and TFs made of ternary nitride alloys, i.e., $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$. In Fig. 4, we show the values of the R_B coefficient in $Al_xGa_{1-x}N$ TFs and $In_xGa_{1-x}N$ QWs grown on GaN substrates that, have been obtained using linear elasticity (dashed lines) and third-order elasticity (solid lines). We observe that the discrepancies between the results obtained using third-order elasticity and linear elasticity are proportional to the magnitude of ε_{xx}. Interestingly, these discrepancies vanish when Al content in $Al_xGa_{1-x}N$ TFs or In content in $In_xGa_{1-x}N$ QWs are smaller than 0.2. Thus, for these strained layers, the R_B coefficient can be regarded as a strain-independent quantity. This effect originates from different values of the elastic constants for binary nitride semiconductors, causing opposite strain dependences of the R_B coefficient in GaN compared to InN and AlN [14]. The R_B coefficient increases significantly with ε_{xx} in AlN and InN, while it decreases in GaN [14], and it is therefore obvious that for certain $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ alloys, the R_B coefficient does not depend on ε_{xx}.

In Fig. 5, we show the R_B coefficient in $Al_xGa_{1-x}N$ QWs grown on AlN substrates and and in $In_xGa_{1-x}N$ TFs grown on InN substrates. The discrepancies between the results obtained using linear elasticity (dashed lines) and third-order elasticity (solid lines) are not proportional to the in-plane strain. Moreover, we observe the crossing of the results obtained using linear elasticity and nonlinear elasticity for $Al_xGa_{1-x}N$ QWs with Al content around 0.1 and $In_xGa_{1-x}N$ TFs with In content around 0.35. This unusual effect originates from opposite strain dependences of the R_B coefficient in GaN, compared to InN and AlN [14].

4. Conclusions

We have studied the R_B coefficient in group-III nitride QWs and TFs using the third-order elasticity theory. We have shown that the R_B coefficient in four material systems, i.e., AlN TFs grown on $Al_xGa_{1-x}N$ substrates, GaN QWs grown on $Al_xGa_{1-x}N$ substrates, GaN TFs grown on $In_xGa_{1-x}N$ virtual substrates, and InN QWs grown on $In_xGa_{1-x}N$ virtual substrates, depends significantly on the lattice misfit between the strained layers and the substrates, which cannot be described by the linear theory of elasticity. The R_B coefficient in most of QWs and TFs made of $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$ alloys significantly depends on the in-plane strain, which is reflected by the observed discrepancies between the results obtained using third-order elasticity and linear elasticity. These discrepancies are proportional to the magnitude of the in-plane strain for $Al_xGa_{1-x}N$ TFs and $In_xGa_{1-x}N$ QWs grown on GaN substrates and they vanish when Al or In content is smaller than 0.2. For $Al_xGa_{1-x}N$ QWs grown on AlN substrates and $In_xGa_{1-x}N$ TFs grown on InN substrates, we find that the discrepancies between the results obtained using third-order elasticity and linear elasticity are not proportional to the in-plane strain. Unusual behaviour of the R_B coefficient in group-III nitride alloys originates from the different values of the elastic constants for the binary nitride semiconductors, causing the opposite dependences of the R_B coefficient on the in-plane strain for GaN compared to InN and AlN [14]. The presented results should prove useful for experimental studies of strain-related phenomena in nitride layers and for modelling of nitride quantum structures and devices [12, 13, 24].

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