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Nonlinear macroscopic polarization in GaN/Al$_x$Ga$_{1-x}$N quantum wells

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We present experimental evidence of the nonlinear behavior of the macroscopic polarization in GaN/Al$_x$Ga$_{1-x}$N quantum wells. This behavior is revealed by determining the barrier-well polarization difference as a function of applied hydrostatic pressure. The polarization difference and corresponding built-in electric field in the wells increase with applied pressure at a much higher rate than expected from the linear model of polarization. This result, universally observed in the quantum well structures with different AlN mole fraction in the barriers, is explained by the nonlinear dependence of the piezoelectric polarization in GaN and AlN on the strain generated by pressure. *© 2002 American Institute of Physics.* [DOI: 10.1063/1.1483906]

Polarization-induced electric fields have a detrimental effect on the electrical and optical characteristics of GaN-based quantum well (QW) devices with wurtzite lattice configuration. In short-wavelength laser diodes, these fields increase the threshold current and redshift the emission wavelength.[1] In emerging long-wavelength structures utilizing intersubband transitions, the fields increase the intersubband relaxation time and reduce the effective barrier height.[2] To utilize the effects of polarization-induced fields in device design in a controllable way, one needs to be able to quantify these fields with good precision. Although significant advances were made in the last few years in the theory of macroscopic polarization in III–V nitrides,[3] some issues are still awaiting clarification. One of them is the effect of alloy composition and strain on the polarization. Original investigations assumed that piezoelectric coefficients and spontaneous polarization in nitrides are insensitive to these parameters.[1,4] However, Shimada *et al.*[5] predicted theoretically that the piezoelectric coefficients of GaN, AlN, and BN strongly depend on volume conserving strain. In agreement with this prediction, we demonstrated experimentally that the piezoelectric coefficients in In$_x$Ga$_{1-x}$N/GaN QWs significantly depend on the strain.[6] We have also suggested that volumetric as well as volume conserving components of strain affect these coefficients. Recently, Bernardini and Fiorentini investigated theoretically the effects of strain and composition on macroscopic polarization in III–V nitrides, and showed that in addition to the nonlinearity in the piezoelectric component of polarization, the spontaneous polarization is also nonlinear with respect to composition.[7]

In this work, we provide experimental evidence of the nonlinear polarization response of GaN/Al$_x$Ga$_{1-x}$N quantum wells to strain. To modify the strain in the wells and in the barriers, we apply hydrostatic pressure to the samples. The strain generated by pressure increases the built-in electric field in the wells, which is manifested in a pressure dependent Stark shift of the photoluminescence (PL) emission peak. The values of well–barrier polarization difference ($P_w - P_b$) and corresponding electric field are obtained from the PL peak energies of samples with varying well width. Our results show that the polarization difference increases with pressure at a much higher rate than expected from the conventional linear model. This finding, made for the samples of different AlN mole fraction in the barriers, suggests a nonlinear character of the strain response of the macroscopic polarization in GaN/Al$_x$Ga$_{1-x}$N QWs.

The GaN/Al$_x$Ga$_{1-x}$N QW structures used in this work were grown on (0001) sapphire substrates by plasma-assisted molecular-beam epitaxy. Details of the growth procedure have been reported previously.[8] We investigated three different samples with similar geometry and 5.2 nm Al$_x$Ga$_{1-x}$N barriers with $x = 0.2$, 0.5, and 0.8, respectively. Each sample has a combination of four GaN QWs 1.8, 2.9, 3.9, and 4.9 nm thick. The QW structures grown on 0.6–0.8 μm GaN layers are nominally undoped.

The PL was excited by the third harmonic (265 nm) of a self-mode-locked Ti:Sapphire laser with 100 fs pulse output. The excitation intensity was kept at a low level of ~2 W/cm^2. The PL emission was collected in a backscattering geometry and detected with a 0.25 m spectrometer and charge coupled device camera. Time-resolved PL measurements with a resolution of ~0.8 ns were obtained with a fast photomultiplier tube and digital oscilloscope in accumulation mode. To apply pressure to the samples, they were cut and polished to a $70 \times 70 \times 30\ \mu m^3$ size, and loaded into a diamond anvil cell filled with liquid argon as a pressure transmitting media.[6] All PL measurements were performed at 35 K.

Figure 1 shows a typical pressure dependence of the PL peak energies in the sample with Al$_{0.5}$Ga$_{0.5}$N barriers. The pressure coefficients (dE/dp) of the QW PL peak are much smaller than that of GaN (~39 meV/GPa) and they decrease with increasing well width from 26.2 meV/GPa in the 1.8 nm well to only 2.9 meV/GPa in the 4.9 nm well. A similar trend is observed in the samples with $x = 0.2$ and 0.8 in the barriers. In the sample with Al$_{0.8}$Ga$_{0.2}$N barriers, the 4.9 nm well

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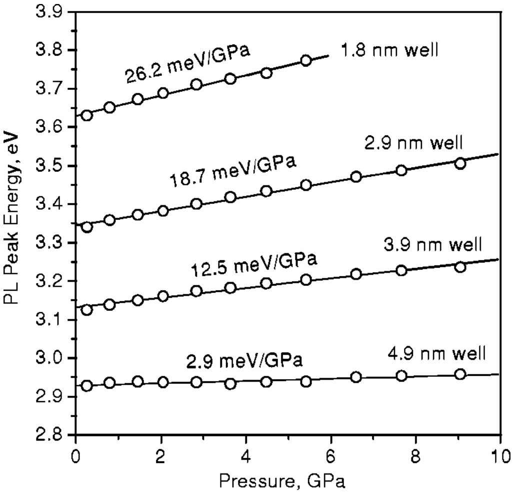

FIG. 1. Pressure dependence of the QW PL peak energies in the sample with $Al_{0.5}Ga_{0.5}N$ barriers. The lines are linear fits to the experimental points. Pressure coefficients are shown above the lines.

shows a record low $dE/dp = -7.2$ meV/GPa.

Figure 2 shows the pressure dependence of PL decay time in the sample with $Al_{0.5}Ga_{0.5}N$ barriers. We observe a significant increase of the decay time with applied pressure, which is more pronounced in the wider 3.9 nm well. The decay time constant increases from 60 to 140 ns when pressure increases from 1 atm to 8 GPa.

The experimental results just described are quite similar to the observations made in our previous work on $In_xGa_{1-x}N$/GaN QWs,[6] and provide additional evidence on the nonlinear behavior of the polarization in the III–V nitrides. As in the case of $In_xGa_{1-x}N$/GaN QWs, the small values of dE/dp and their well width dependence result from an increase of the built-in electric field with pressure. The decay time increase is due to the increased spatial charge separation in the wells by the electric field leading to the reduction in the electron–hole wave function overlap.[6]

In the following, we provide an analysis of the experimental data aimed at evaluating the magnitude of the built-in electric field at different pressures. Since the field magnitude depends on the sample geometry and distribution of free charges, we concentrate on determining the polarization difference $P_w - P_b$ instead, which defines the electric field F_w in the wells as[9]

$$F_w = \frac{-(P_w - P_b) + \rho}{\epsilon(1 + L_w/L_b)} + \frac{V_s}{L_b + L_w} - \frac{qN_D}{\epsilon}\left[d - \frac{L_b + L_w}{2}\right], \qquad (1)$$

where ϵ is the permittivity of the GaN wells and $Al_xGa_{1-x}N$ barriers (assumed to be independent of pressure in this work), $L_{w,b}$ are the cumulative thicknesses of the well and the barrier layers, ρ is the two-dimensional photogenerated charge density in the wells, V_s is the surface barrier potential determined as in Ref. 9, $N_D \approx 10^{17}\ \mathrm{cm}^{-3}$ is the background doping concentration, and d is the distance from the barrier–buffer interface to the well where the field is calculated. To find $P_w - P_b$ as a function of pressure the experimentally measured PL peak energy variation with well width was fitted with the calculated dependence of the $e_1 - hh_1$ transition

$$E_{e_1 - hh_1} = E_{\mathrm{GaN}} + E_{e_1} + E_{hh_1} - E_{\mathrm{ex}}, \qquad (2)$$

where E_{GaN} is the GaN band gap energy, E_{e_1} and E_{hh_1} are the confinement energies, and E_{ex} is the exciton binding energy. The GaN and $Al_xGa_{1-x}N$ band gap energies at each pressure were found using the deformation potentials of GaN and AlN given in Ref. 10. The electron and hole confinement energies in the presence of F_w were found using the method described in Ref. 11. The binding energies of the confined excitons subjected to an electric field were calculated using the approach developed by Leavitt and Little.[12] The only adjustable parameter used in the fit is $P_w - P_b$. Figure 3 shows the fit to the measured PL peak energies in the different samples at a pressure of 5 GPa. The good agreement between the fit and the experiment highlights the importance of the built-in electric field in shaping the well width dependence of the ground-state energy.

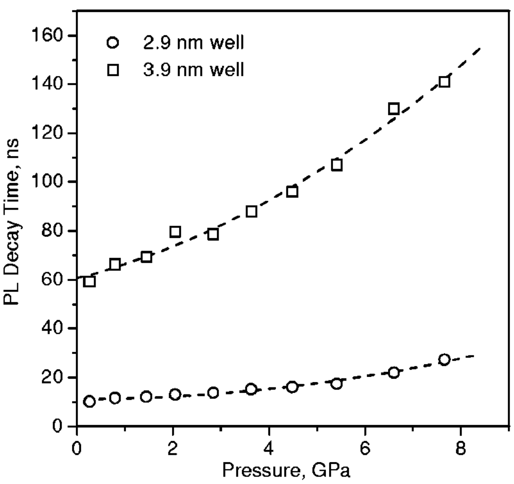

FIG. 2. PL decay time as a function of pressure in the sample with $Al_{0.5}Ga_{0.5}N$ barriers. The measurements were made at excitation density of $\sim 2\ \mathrm{W/cm^2}$. The dashed lines serve as guides for the eye.

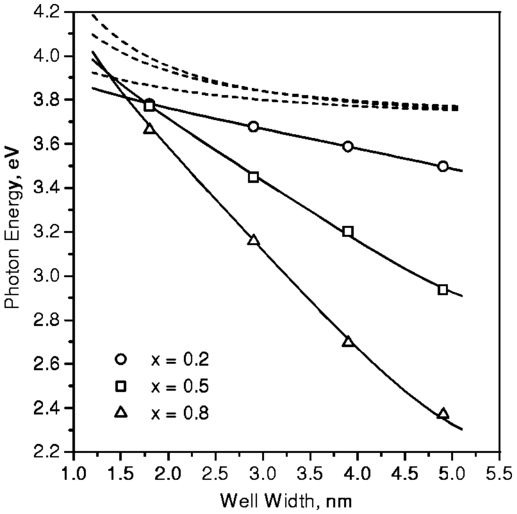

FIG. 3. Well width dependence of the PL peak energy at 5 GPa. Open symbols show the experimental points; solid lines are the fits to the experimental data obtained with $P_w - P_b$ being the only adjustable parameter; dashed lines—$e_1 - hh_1$ transitions calculated for the field-free case.

Using the procedure described herein, we determined the polarization difference $P_w - P_b$ and resulting electric field in the 2.9 nm wells for all samples. The results of this analysis are presented in Fig. 4. In every sample, $P_w - P_b$ signifi-

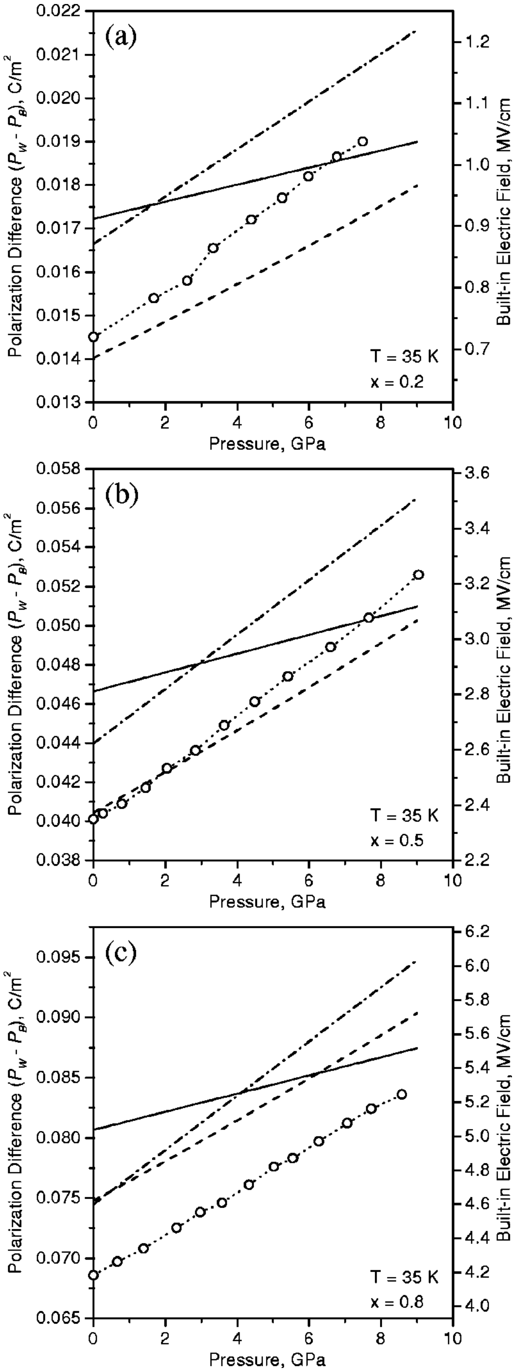

FIG. 4. Pressure dependence of $P_w - P_b$ and corresponding electric field in 2.9 nm GaN/Al$_x$Ga$_{1-x}$N QWs with $x=0.2$ (a), 0.5 (b), and 0.8 (c). The experimental points shown by the circles were obtained from the fit to the PL data as shown in Fig. 3.

cantly increases with pressure, resulting in an increase of the built-in field of 0.32 MV/cm, 0.76 MV/cm, and 1.01 MV/cm in the samples with $x=0.2$, 0.5, and 0.8, respectively at 8 GPa. Figure 4 also shows the results of the calculation of the pressure dependence of $P_w - P_b$ using model predictions. The solid lines correspond to $P_w - P_b$ calculated with the conventional model of polarization.[1] This model predicts significantly larger values of $P_w - P_b$ at atmospheric pressure and a much smaller change with pressure than experimentally determined. The dashed-dotted lines are the results of calculations where only the volume-conserving strain dependence of the GaN and AlN piezoelectric coefficients is taken into account.[5] This model shows a better match with the experimental data than the conventional model. This is in agreement with the recently reported work by Perlin *et al.*,[13] where the pressure dependence of PL in GaN/Al$_{0.13}$Ga$_{0.87}$N QWs was found to be adequately described by the volume-conserving strain dependence of the piezoelectric coefficients. And finally, the dashed line in Fig. 4 shows the result of calculations where the nonlinear behavior of both the spontaneous and piezoelectric polarizations were taken into account using the results of Bernardini and Fiorentini.[7] We considered here only the changes in piezoelectric polarization due to hydrostatic compression of the (ideal) crystal and due to the increase of the internal parameter u with pressure.[14] The spontaneous polarization bowing was included at $p=0$.[7] Although this is only an approximation of the theory developed in Ref. 7, this model also predicts the slope of the pressure dependence of $P_w - P_b$ significantly larger than that of the linear model.

In summary, we have presented conclusive experimental evidence of nonlinear macroscopic polarization in the GaN/Al$_x$Ga$_{1-x}$N QWs with different AlN mole fraction in the barriers. We show that the linear model of polarization does not describe the experimentally observed variation of the polarization and built-in electric field with applied hydrostatic pressure. To provide an accurate description of the macroscopic polarization in GaN/Al$_x$Ga$_{1-x}$N QWs, the nonlinear behavior of the spontaneous and piezoelectric components of polarization should be considered.

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