Interface electronic transition observed by optical second-harmonic spectroscopy in β-GaN/GaAs(001) heterostructures

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Optical second-harmonic spectroscopy was used to probe the interface electronic structure of highly mismatched β-GaN/GaAs(001) heterostructures in the vicinity of the E_0 interband critical point of β-GaN. The resonance energy of both bulk and interface two-photon E_0 transitions from layers between 1- and 100-nm thickness are identical, indicating the absence of appreciable amounts of strain and electric fields in this materials system. This finding is in striking contrast to observations made for other materials systems, including ZnSe/GaAs and SiO_2/Si, where large shifts of several 10 meV with respect to the bulk values have been found. [S0163-1829(98)06804-0]

At abrupt crystalline heterointerfaces, changes in optical resonance energies compared to the respective bulk arise from the structural and chemical dissimilarity of the constituent materials. The former results in lattice- and thermal-mismatch-induced strain, while the latter induces interfacial dipole layers via the different electronegativities of the constituent atoms at the heterointerface.[1]

Second-order nonlinear optical probes are well suited for studying the electronic and optical properties of buried heterostructure interfaces, where conventional surface-physics probes cannot be used.[2–8] By capitalizing on crystal symmetry, optical second-harmonic (SH) and sum-frequency spectroscopy have been used successfully for probing strain, defect states, electric fields, and electronic transitions at the SiO_2/Si interface,[9–12] and other important heterojunctions including CaF_2/Si,[8] GaP/Si[7] and ZnSe/GaAs.[5,6] In the case of GaP/Si, we observed a redshift of $\sim$70 meV of the silicon E_1 transition at the heterointerface.[7] This experimental result is in agreement with the interfacial dipole model, since bonds in the nonpolar Si crystal are weakened by local electron transfer to the polar GaP at the heterojunction. These weakened bonds give rise to an interface resonance that is redshifted with respect to the bulk resonance of Si.

This paper reports on optical SH spectroscopy studies of β-GaN/GaAs(001) heterostructures of differing thicknesses. The reasons for studying this materials system are twofold: (i) the large (20%) lattice-mismatch is expected to give rise to a high and strongly thickness-dependent excess strain at the interface, and (ii) the large electronegativity difference (dielectric mismatch) between β-GaN and GaAs is expected to lead to a high excess charge at the interface.

Cubic GaN films of 1–100-nm thickness were grown on semi-insulating GaAs(001) by molecular-beam epitaxy using a high-voltage ($\simeq$1.5 kV) plasma glow discharge N source as described in Ref. 13. Their structural, morphological, electronic, and optical properties have been investigated and compared to those measured for thick ($\simeq 1$ μm) films by several techniques including *in situ* reflection high-energy electron diffraction,[13–15] high-resolution transmission electron microscopy (HREM),[16,15] atomic-force microscopy,[17,15] x-ray diffraction,[14] Raman spectroscopy,[18] and photoelectron emission spectroscopy.[19] The results of these studies can be summarized as follows. All the β-GaN films under consideration are connected epitaxial layers with rms roughnesses of 0.15–0.5 nm (the roughness increases with increasing thickness). Both their lateral and vertical lattice constants at room temperature are found to be 0.451 nm, regardless of their thickness, which is identical to the value obtained for thick films. This independence of lattice constant on thickness seems to imply that all layers are completely relaxed. Note, however, that the experimental accuracy worsens with decreasing thickness, so that significant excess strain could be contained within the thinnest layer studied here. Note also that none of these experiments gives direct access to the electronic properties of the interface itself.

For second-harmonic generation dispersion measurements, a beam consisting of 100-fs pulses at a repetition rate of 76 MHz generated by a mode-locked Ti:sapphire laser was focused on the sample to a 10-μm-diameter spot at a 45° angle of incidence. In all experiments, we detected the p-polarized reflected SH response produced by excitation with p-polarized fundamental radiation of 4-mW average power. The details of the experimental setup are given in Ref. 7.

The dispersion of the nonlinear susceptibility $\chi^{(2)}$, describing the optical SH response, reflects the electronic band structure of the system. In our experiments, the SH photon energy is chosen to be near the direct band gap of β-GaN, so that the dominant contribution to $\chi^{(2)}$ arises mainly from

two-photon transitions between the top valence band $|v\rangle$ and the lowest conduction band $|c\rangle$ at the Γ point in the Brillouin zone. If the fundamental frequency ω is far from resonance, $\chi^{(2)}$ may be written as[12]

$$\chi^{(2)}_{ijk}(-2\omega;\omega,\omega)\sim\frac{\langle v|r_i|c\rangle}{(2\hbar\omega-E_{vc}-i\hbar\gamma_{vc})}C(\omega)+\chi^{(2)}_{\mathrm{nr}}, \tag{1}$$

where r_i is the Cartesian coordinate operator, E_{vc} is the energy separation between electronic states $|v\rangle$ and $|c\rangle$, γ_{vc} is half of the linewidth of the $|v\rangle\rightarrow|c\rangle$ transition, and $C(\omega)$ contains matrix elements and a frequency denominator that change very little for the frequency range investigated. $\chi^{(2)}_{\mathrm{nr}}$ is a nonresonant or background contribution to the total SH response.

GaAs and β-GaN are zinc-blende crystal structures, and therefore lack inversion symmetry. Both crystals have a single bulk second-order susceptibility component, $\chi^{(2)}_{xyz}$, whose contribution to the output radiation is highly anisotropic, reflecting the twofold symmetry of bonding on {001} planes. Additionally, isotropic nonlinear susceptibility components such as $\chi^{(2)}_{zxx}$, $\chi^{(2)}_{xzx}$, and $\chi^{(2)}_{zzz}$ are permitted at the interfaces of the β-GaN/GaAs heterostructure, where the inversion symmetry is broken with respect to the surface normal (z axes). For very thin films [$d\ll\alpha^{-1}$ (GaN), where α is the absorption coefficient], both the buried β-GaN/GaAs interface and the front β-GaN surface contribute to the isotropic SH response. For thicker overlayers, the SH field of the front β-GaN surface will dominate due to absorption of the SH radiation in both the β-GaN overlayer and GaAs substrate. Finally, isotropic interface and anisotropic bulk SH contributions were separated by performing a Fourier analysis of the SH rotational anisotropy, as outlined in Ref. 7.

The energy position and the linewidth of the bulk and interface resonance give, in principle, important information about residual elastic strain in the epilayer, the presence of an interface dipole layer,[7] and surface microroughness. The interface and bulk SH spectra obtained from the β-GaN layers under investigation are shown in Figs. 1 and 2 as a function of SH photon energy. As shown in Fig. 2(a), the bulk SH intensity from the GaAs(001) substrate exhibits no apparent resonances in the range 3.0–3.5 eV. For all β-GaN layers investigated, both the interface and the bulk SH spectrum exhibit a resonance feature at 3.24 ± 0.02 eV, which corresponds to the bulk E_0 transition of β-GaN [see Figs. 1(a) and 2(a)]. The error margin represents the average statistical confidence interval of the Lorentzian line shape fits. The broadening of the interface electronic transitions with increasing thickness (see Fig. 1) is presumabely related to the increasing surface roughness of the films (namely, 0.15 and 0.5 nm for the 1- and 100-nm-thick films, respectively). Most important, however, is the absence of any detectable shift of both bulk and interface resonance within experimental accuracy indicating that the interface is possibly free of strain ($<0.5\%$) and excess charge (dipole <10 meV).

The absence of any detectable homogeneous strain in these thin films is, at first glance, surprising in view of the huge lattice mismatch of $20\pm0.2\%$ between β-GaN and GaAs. However, the HREM studies mentioned above have conclusively shown that the mismatch is entirely accommodated by a unique interface configuration in which five GaN lattice planes are spatially correlated with four GaAs lattice planes, as depicted schematically in Fig. 3. This kind of interface configuration is a coincidence lattice which is determined by the ''magic mismatch'' ($a_{\mathrm{GaN}}/a_{\mathrm{GaAs}}=4/5$) between β-GaN and GaAs.[16] The interface depicted in Fig. 3 is obtained by rigidly putting β-GaN on GaAs(001) which would create, radially as well as angularly, tensile bond dis-

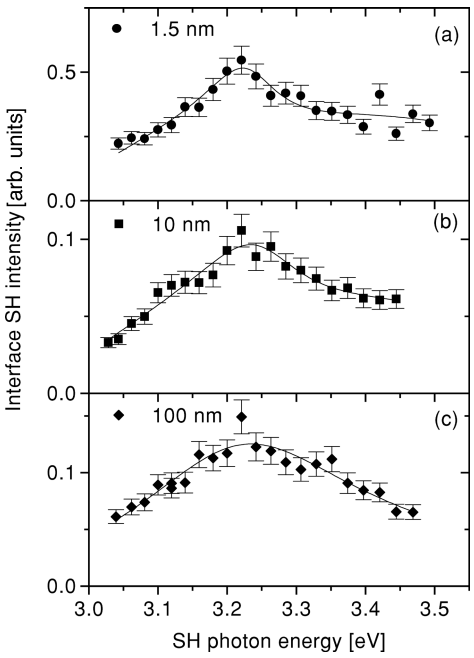

FIG. 1. Interface SH spectra from β-GaN/GaAs(001) heterostructures with different thicknesses of the β-GaN overlayer. The solid lines indicate line-shape fits assuming an asymmetric Lorentzian resonance.

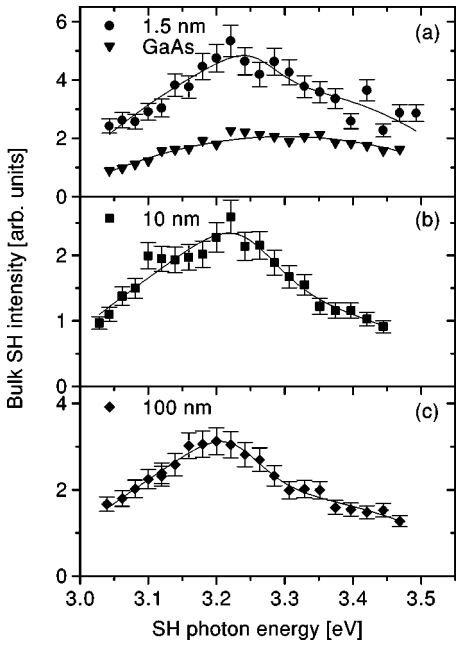

FIG. 2. Bulk SH spectra from the same samples used in Fig. 1 and from a GaAs(001) wafer. The solid lines indicate line-shape fits assuming an asymmetric Lorentzian resonance.

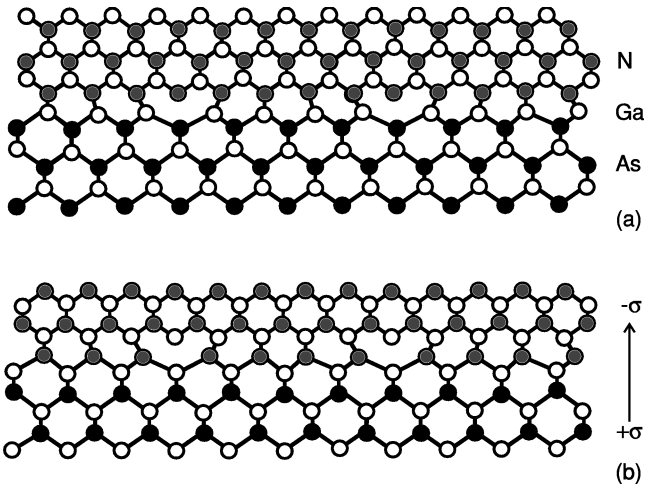

FIG. 3. Scheme of the interface bonding arrangement and dipole layer at the β-GaN/GaAs(001) heterojunction along the (a) $[1\bar{1}0]$ and (b) [110] directions. This scheme is obtained by rigidly putting β-GaN onto GaAs, and neglecting interface relaxation and dislocation reconstruction.

tortions. However, three-dimensional valence force-field calculations show that these large local distortions constitute an enormous driving force for interface relaxation, proceeding such that the interface bonds eventually reach alternatively compressive and tensile strain state which, within each unit cell of the coincidence lattice, compensate for each other. Analogously, the respective charge excess and deficit associated with the perpendicular N- and Ga-terminated edge dislocations within each unit cell (cf. Fig. 3) counterbalance each other. Note that the thermal mismatch between β-GaN and GaAs, if accommodated elastically, would lead to a compressive strain within the β-GaN layer of 0.25%. Such a strain would, if present, lead to a shift of the E_0 transition of at most 10 meV when considering the elastic constants and band-edge deformation potentials of β-GaN,[20] which is within our experimental uncertainty. Finally, we have to consider the possible presence of an interfacial dipole layer. Since the average electronegativities ($\chi_{\rm av}=0.5[\chi_A+\chi_B]$) are different on either side of the β-GaN/GaAs heterointerface, charge transfer between β-GaN ($\chi_{\rm av}=2.43$) and GaAs ($\chi_{\rm av}=2.00$) will take place inevitably. For the β-GaN/GaAs(001) heterojunction the interfacial bonding arrangement that is the basis of the localized dipole model is depicted in Fig. 3. At the buried β-GaN/GaAs heterointerface, negative charges are transferred from the GaAs side due to the higher $\chi_{\rm av}$ of β-GaN as compared to GaAs, which potentially produces a dipole field $\vec{p}=(e\sigma/\epsilon)\hat{z}$ at the heterointerface of the order of 10^7 V/cm ($\sigma\sim10^{14}$ cm^{-2}). The idealized interfacial atomic arrangement, as depicted in Fig. 3, will of course not be stable in the presence of such huge fields, but the interface will reconstruct. However, given the kinetic limitations for any realistic growth process, finite residual interface fields should be expected to remain at the interface which might be as large as the fields intentionally incorporated in *p-n* junctions[21] and piezoelectric layers.[22] This residual interfacial dipole field would enhance the strength of the Ga-N bonds on the β-GaN side of the heterointerface, corresponding to a dipole-induced compressive strain. Quantitatively, the above-mentioned residual field would correspond to a dipole potential of about 20 meV,[1] and a dipole-induced compressive strain of 2%, resulting in a blueshift of $\simeq$60 meV. Our measurements, however, set the value for the interface dipole to at most 10 meV. This finding demonstrates that the above expectation is not, in general, valid for any interface. Apparently, the β-GaN/GaAs(001) interface strongly reconstructs, and thus reduces the interface dipole to essentially zero within experimental sensitivity. There are thus three important consequences resulting from this type of large-misfit heterointerface: (i) it promotes perfect lattice matching in the sense that the overlayer is globally strain free, (ii) it produces an ordered array of interfacial dislocations whose net charge is zero, and (iii) it facilitates interface reconstruction to reduce fields induced by the dielectric mismatch. These conditions are guaranteed by the magnitude of the associated excess strain and charge, in contrast to low-mismatch systems such as ZnSe/GaAs(001), where the driving forces are too weak for ever reaching strain and charge neutrality. In this latter system, for example, the difference between the $\chi_{\rm av}$'s is analogous to β-GaN/GaAs, and additionally the relative band gaps follow the $\chi_{\rm av}$'s as well. In the context of the interfacial dipole model, this means that ZnSe/GaAs heterostructures are expected to exhibit an interface resonance which is blueshifted with respect to the bulk E_0 transition in ZnSe, which in fact was observed in the three-wave-mixing experiments by Yeganeh *et al.*[5,6]

In conclusion, we investigated the nonlinear optical response from β-GaN/GaAs heterostructures. The absence of any detectable shift of the E_0 interband transition suggests that this highly lattice- and dielectric-mismatched interface can be very efficiently reconstructed such that both strain and charge neutrality are established. This phenomenon is likely to be triggered by the magnitude of the associated excess strain and charge, in contrast to low-mismatch systems such as ZnSe/GaAs(001) where the driving forces are too weak to ever reach strain and charge neutrality.

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