Fermi level shift in GaInNAsSb/GaAs quantum wells upon annealing studied by contactless electroreflectance

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Contactless electroreflectance (CER) spectroscopy has been applied to study band bending in GaInNAsSb/GaAs quantum well (QW) structures. It has been observed that CER features significantly changes upon annealing: the period of GaAs-related Franz-Keldysh oscillations increases; intensities of excited QW transitions rose compared to the intensity of the fundamental QW transition. The observed changes in CER spectra have been explained by a shift of the Fermi level in the GaInNAsSb layer: the defect states in as-grown GaInNAsSb tend to pin the Fermi level at an energy characteristic for these defects; annealing removes defects from this material and effectively shifts the Fermi level to the conduction band. © *2007 American Institute of Physics*.
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Dilute nitride III-V alloys (GaNAs, GaInNAs, and GaInNAsSb) are promising materials for 1.3 and 1.55 μm telecommunication optoelectronic devices grown on GaAs substrates.[1] The role of nitrogen in GaAs is twofold: nitrogen causes the bulk band gap to decrease and, concurrently, reduces the lattice constant and strain of III-V-N materials when grown upon GaAs.[2] Unfortunately, nitrogen also generates many structural defects which lead to energy states inside the band gap and is responsible for the poor optical quality of III-N-V alloys. Postgrowth *ex situ* annealing typically improves the optical properties of III-N-V alloys and is a standard step in the fabrication of dilute nitride-based lasers. However, the changes that occur during annealing are complex and not fully understood. Questions are then raised: Can the defect states pin the Fermi level? How does annealing influence the position of Fermi level in dilute nitrides? Some answers for these questions can be determined by electromodulation spectroscopy.

Electromodulation (EM) spectroscopy (photoreflectance and electroreflectance) is known as an excellent tool to investigate both the fundamental and higher order quantum well (QW) transitions.[3–5] In addition, for samples with a built-in electric field (usually $F > 20$ kV/cm), EM spectra exhibit oscillatory patterns for bulklike transitions, i.e., Franz-Keldysh oscillations (FKOs).[3,6] The electro-optic energy, which corresponds to the period of FKOs, is related to the amplitude of built-in electric fields. In semiconductor structures, the built-in electric fields are produced by Fermi level pinning at the surface and interfaces. The simplest structure to study Fermi level pinning is the "Van Hoof structure."[7] Samples investigated in this letter can be treated as modified Van Hoof structures since a single GaInNAsSb QW was grown in the region of the undoped GaAs layer, see Fig. 1. The purpose of this letter is to investigate the band bending for modified Van Hoof structures and its change upon annealing by measuring GaAs-related FKOs with contactless electroreflectance (CER) spectroscopy.

The $Ga_{0.92}In_{0.08}N_{0.025}As_{0.9}Sb_{0.075}$/GaAs QW samples used in this study were grown on *n*-type (100) GaAs substrates by solid-source molecular beam epitaxy (MBE) in a Varian Mod Gen-II system. The structure consists of a 7.5 nm $Ga_{0.92}In_{0.08}N_{0.025}As_{0.9}Sb_{0.075}$ QW grown on a 300 nm GaAs buffer capped by a 50 nm GaAs layer. The GaInNAsSb QW was grown at a substrate temperature of 440 °C measured by pyrometer. The background impurity concentration (H, O, C, and B) in our materials is known to be below 1×10^{17} cm^{-3}.[8] A piece of this sample was annealed at 780 °C for 60 s. Other details of the growth as well as the structural characterization are given elsewhere.[9] Samples for CER measurements were mounted in a capacitor with a semitransparent electrode made from a copper-wire mesh. This electrode was kept at a distance of ~0.2 mm from the sample surface while the sample itself was fixed on the bottom copper electrode. A maximum peak-to-peak alternating voltage of ~1.8 kV was applied. Inside the sample the built-in electric field is modulated with the amplitude of few tens of kV/cm since the most voltage drop appears mainly in the air gap between the front electrode and the sample. The frequency of the ac voltage was 285 Hz.

Figures 2(a) and 2(b) show the CER spectra for the as-grown and annealed GaInNAsSb/GaAs QWs, respectively. The spectra are dominated by the GaAs bulklike signal with strong FKOs. Below the GaAs signal, CER features associated with the optical transitions in GaInNAsSb/GaAs QW are clearly visible. They were analyzed using the low-field electromodulation Lorentzian line shape functional form[3] and their identification was possible due to a series of calculations which have been described in details in Ref. 5. The dashed lines in Fig. 2 represent the modulus of individual CER resonances (individual QW transitions) and the notation *kl*H (L) denotes the transition between the *k*th heavy-hole (light-hole) valence subband and the *l*th conduction subband.

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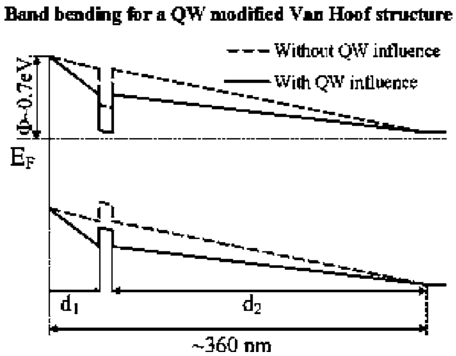

FIG. 1. Sketch of band bending in GaAs-based Van Hoof structures with a GaInNAsSb QW in the region of undoped GaAs layer. The dashed line corresponds to a situation when the band bending is not modified by the QW whereas the solid line corresponds to a situation when the QW influences band bending in this structure. Since the GaAs cap and buffer layers are undoped and high quality, it is assumed that the electric field in these layers is constant and results form the Fermi level pining at GaAs surface, GaInNAsSb QW, and n-type GaAs substrate.

It is seen that all QW transitions blueshift due to annealing [compare the moduli in Figs. 2(a) and 2(b)]. The blueshift of the QW transitions is a phenomenon which is expected for this system[1] and will be discussed elsewhere. In addition, the relative intensities of QW transitions change compared to the intensities for the as-grown sample. For example, the 22H transition is stronger than the 11H transition for the annealed sample, as seen in Fig. 2(b). The intensities of QW transitions observed in EM spectroscopy depend on (i) electron-hole overlaps for QW transitions and (ii) their sensitivity to the electric field. The two components vary with the built-in electric field, and exists inside the structure. Thus, the observed change in the intensity of QW transitions is an indirect evidence that the built-in electric field changes upon annealing. The built-in electric field can be investigated directly for these samples since GaAs signal exhibits clear FKOs.

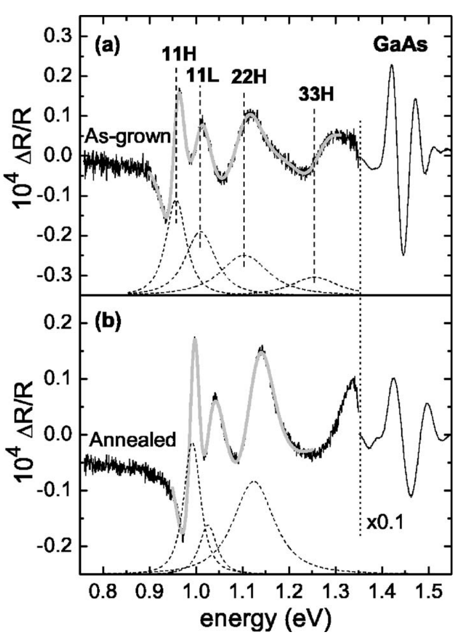

FIG. 2. Room temperature contactless electroreflectance spectra for the as-grown (a) and annealed (b) $Ga_{0.92}In_{0.08}N_{0.025}As_{0.9}Sb_{0.075}$/GaAs single QWs (thin solid lines) together with the fitting curve (thick solid lines) and the moduli of individual CER resonances (dashes lines).

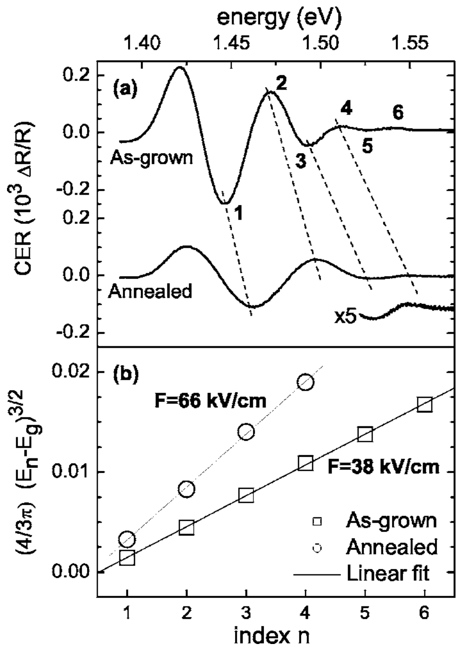

FIG. 3. Room temperature contactless electroreflectance spectra for the as-grown and annealed $Ga_{0.845}In_{0.08}N_{0.025}As_{0.975}Sb_{0.075}$/GaAs single QWs in the vicinity of GaAs-related absorption (a) together with the analysis of Franz-Keldysh oscillations (b).

Figure 3(a) shows the CER spectra for as-grown and annealed GaInNAsSb/GaAs QWs in the vicinity of GaAs-related absorption. The increase of the FKO periodicity after annealing is clearly seen. The extrema of the FKOs are given by

$$n\pi = \varphi + \left(\frac{4}{3}\right)\left(\frac{e^2\hbar^2F^2}{2\mu}\right)^{3/2}, \tag{1}$$

where n is the index of the nth extrema, φ is an arbitrary phase factor, E_n is the energy of the nth extrema, and E_0 is the energy gap, and the electro-optic energy is given by

$$(\hbar\theta)^3 = \frac{e^2\hbar^2F^2}{2\mu}, \tag{2}$$

where μ is the reduced interband effective mass for the electron and heavy-hole pair in the direction of electric field. If μ is known [μ is $0.055m_0$ for (100) direction in GaAs after Ref. 11] the built-in electric field F can be directly evaluated from a plot of $(4/3\pi)(E_n-E_g)^{3/2}$ as a function of index n [see Fig. 3(b)]. It has been found that the slope yields electric fields of 38 and 66 kV/cm for as-grown and annealed samples, respectively.

For standard Van Hoof structures, the built-in electric field can be estimated with the knowledge of the thickness of GaAs epilayers and the Fermi level pining at the GaAs surface and at the GaAs (buffer)/GaAs (n-type substrate) interface,[6] as shown in Fig. 1. However, in this case, the measured electric fields are much higher than previous estimations [38 kV/cm (as grown) and 66 kV/cm (annealed) versus 19 kV/cm]. It means that the QW modifies band bending in this system. Neglecting the small band bending near the surface and interface due to this small background doping, the built-in electric field in the GaAs cap and buffer layers can be assumed to be uniform[6] as in Fig. 3, the potential difference between GaAs surface and GaAs/(GaAs n-type substrate) interface Φ is given by following formula

$\Phi \approx F_1 d_1 + F_2 d_2$, where F_1 and F_2 are the built-in electric field in the GaAs cap and buffer layers, respectively, and d_1 and d_2 are the thickness of GaAs cap and buffer layers, respectively. For (100) GaAs surface the Φ is known to be $\sim$0.7 eV at room temperature.[6] The founded electric field should be connected with the cap or the buffer layer. The CER signal usually originates from the section of sample which is close to the surface since the external electric field modulates band bending at the surface mainly.[12] Therefore, the measured electric field is attributed to the GaAs cap layer in these samples. According to equation $\Phi \approx F_1 d_1 + F_2 d_2$, the electric fields in GaAs buffer layer have been found to be 17 and 12 keV/cm for the as-grown and annealed samples, respectively. In this regime of electric field any strong FKOs are rather not expected.[3,6] In the low-field regime a Lorentzian-like or Gaussian-like resonance at 1.42 eV is expected.[3] In our spectra such a resonance is not resolved because of weak intensity due to weaker electromodulation in the buffer layer[12] and some superimposes with the strong cap-related FKO signal.

Assuming the Fermi level at the GaAs surface does not change after annealing,[13] it has been concluded that the Fermi level in the region of GaInNAsSb QW shifts towards the conduction band upon annealing, as shown in Fig. 1. The annealing process changes the type of GaInNAsSb material from *p*-like to *n*-like (or enhances the *n*-like character of GaInNAsSb material). Similar conclusion have been obtained by Kurtz *et al.*[14] for nominally undoped GaInNAs layers grown by metal organic chemical vapor deposition (MOCVD). The authors have correlated the observed type conversion with both nitrogen and hydrogen concentrations. It is worth mentioning that similar phenomenon is observed for samples grown by the solid-source MBE, which is a hydrogen-free technique. We believe that the same native defects, which appear after the incorporation of nitrogen atoms, can be responsible for this phenomenon in both MOCVD and MBE grown samples. Postgrown annealing is able to remove and/or to passivate these defects. Finally, the charge density in the QW region can change by one magnitude due to structural changes in the GaInNAsSb material only. A diffusion of dopands from the *n*-type substrate to the QW region is possible but cannot explain the observed increase in the electric field since the undoped GaAs buffer layer is 300 nm thick and effectively separates the GaInNAsSb QW from the substrate.

In conclusion, CER spectroscopy has been applied to study band bending in modified Van Hoof structures containing $Ga_{0.92}In_{0.08}N_{0.025}As_{0.9}Sb_{0.075}$ QWs. It has been concluded that GaAs-related FKOs originate primarily from the GaAs cap layer. The magnitude of the built-in electric has been found to increase by 74% upon annealing. This effect has been attributed to a Fermi level shift in GaInNAsSb layer. It has been concluded that the defect states in as-grown undoped GaInNAsSb tend to pin the Fermi at an energy characteristic for these defects. Postgrowth annealing removes defects from this material and effectively shifts the Fermi level to the conduction band.

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