Thin Solid Films 567 (2014) 101–104

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Surface photovoltage and modulation spectroscopy of E_- and E_+ transitions in GaNAs layers

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ARTICLE INFO

Article history:
Received 27 February 2014
Received in revised form 28 June 2014
Accepted 31 July 2014
Available online 7 August 2014

Keywords:
Dilute nitrides
Surface photovoltage
Photoreflectance
Contactless electroreflectance

ABSTRACT

Surface photovoltage (SPV) spectra were measured for $GaN_{0.014}As_{0.986}$ layers at room temperature and compared with room temperature photoreflectance (PR) and contactless electroreflectance (CER) measurements. Spectral features related to E_- and E_+ transitions were clearly observed in SPV spectra at energies corresponding to PR and CER resonances. In this way it has been shown that SPV spectroscopy is an alternative absorption-like technique to study both the E_- and E_+ transitions in dilute nitrides. The observation of E_+ transition in SPV spectra means that it is a direct optical transition at the Γ point of GaNAs band structure which can be explained by the band anticrossing interaction between the localized states of N and the extended conduction band states of the GaAs host.

1. Introduction

GaNAs alloy with a few percent of nitrogen is the prominent member of a specific class of semiconductor materials known as highly mismatched alloys [1,2]. In such alloys the band-gap engineering is achieved by strongly perturbing the host by incorporation of isovalent atoms which significantly differ from host atoms. The isovalent atom (in this case it is nitrogen) dramatically narrows the fundamental band-gap and increases the electron effective mass compared to the host material [1,3–7]. Nitrogen is also responsible for strong carrier localization at low temperatures [8] and formation of native defects [9] in GaNAs alloys.

It has been shown that the electronic band structure of GaN_xAs_{1-x} with a few percent of nitrogen can be described in terms of an anticrossing interaction between the localized states of N and the extended conduction band states of the GaAs host [1,10,11]. This strength of the interaction is described by the off-diagonal element $V_{NM} = C_{NM}\sqrt{x}$ in the band anticrossing (BAC) Hamiltonian given by

$$H_{BAC} = \begin{pmatrix} E_M(k) & V_{NM} \\ V_{NM} & E_N \end{pmatrix} \quad (1)$$

where $E_M(k)$ is the energy dispersion of the lowest conduction band of the III–V host and E_N is the energy of N-related states, all referenced to the top of the valence band of the host (for GaNAs $E_N = 1.65$ eV). x is the nitrogen concentration and C_{NM} is a coupling constant depended on the host matrix (for GaNAs $C_{NM} = 2.7$ eV). The band anticrossing interaction results in formation of two subbands E_- and E_+ with dispersion relations given by

$$E_\pm(k) = \frac{1}{2}\left[E_N + E_M(k) \pm \sqrt{[E_N - E_M(k)]^2 + 4V_{NM}^2}\right]. \quad (2)$$

These subbands are plotted by thin black line in Fig. 1. Also shown in Fig. 1 is the band structure of GaNAs obtained with a more complete 10-band *kp* Hamiltonian that includes 6 valence bands, 2 conduction bands and 2 localized N states, see Refs. [12,13]. It is evident that within this band structure of GaNAs alloy an extra optical transition at the Γ point (E_+ transition) is expected besides the fundamental transition (E_- transition). It was also suggested that the E_+ transition is associated with the presence of a close lying subsidiary, indirect conduction band minimum, which is L band minimum in the GaNAs case [14].

So far the key experimental evidence for the BAC model was provided by the observation of both the E_- and E_+ transitions in photoreflectance (PR) measurements performed at high hydrostatic pressures [1]. Also measurements of energy of E_- transition as a function of the isovalent trap concentration by using photoluminescence or other techniques can confirm the band anticrossing behavior for this band [15–17].

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http://dx.doi.org/10.1016/j.tsf.2014.07.052
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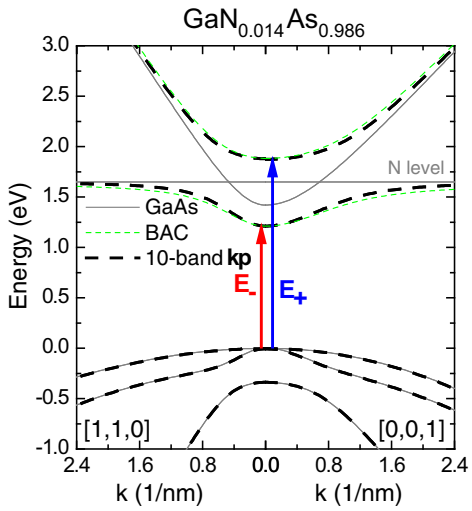

Fig. 1. Band structure of $GaN_{0.014}As_{0.986}$ calculated within the BAC model (thin black lines) and 10-band *kp* model (dashed black lines).

However the observation of E_+ transition seems to be the best evidence for the identification of band anticrossing interaction in the conduction band of dilute nitrides. So far, other absorption-like techniques than PR, which are sensitive to optical transitions at critical points of the band structure, were not applied to study the E_+ transition in GaNAs alloys. In this paper, we show that surface photovoltage (SPV) spectroscopy is a very good tool to study both the E_- and E_+ transitions in GaNAs alloys.

SPV spectroscopy is a well known technique to map the electronic structure of bulk semiconductors near the band edge [18–20]. This technique measures the change in surface potential induced by optically excitation with periodic illumination. The measured potential is produced by carrier redistribution and/or capture of the photoexcited carriers in the surface states. It is a contactless and nondestructive method which can provide information for both the optical absorption transitions and the electronic transport in bulk materials and nanostructures even at room temperature. Recently, SPV was extensively applied to study the band structure of low dimensional heterostructures [21–26]. Also dilute nitrides were investigated by this technique [27–29] but the observation of E_+ transition in SPV spectra was not reported so far for these materials. In this paper we applied SPV spectroscopy to study the E_+ transition in samples where this transition was clearly observed in PR spectra.

2. Experiment

The $GaN_{0.014}As_{0.986}$ layers were grown on (001) semi-insulating GaAs substrates by molecular-beam epitaxy (MBE), using solid Ga, As_2, and Si sources and an N_2 rf plasma source. The target doping concentration for the doped sample is on the order of ~5×10^{17} cm^{-3}, as confirmed in GaAs films. The N composition in the GaNAs layers was adjusted by varying the gas flow rate monitored by partial pressure of 14 amu (active N) in the MBE chamber, as measured with a residual gas analyzer. After an initial GaAs buffer layer was grown at 580–500 °C, a series of annealing steps were performed with As overpressure, followed by the growth of 500 nm thick GaNAs: (Si) layers at 400 °C. Postgrowth annealing was performed at 760 °C for 60 s in N_2 ambient, with a GaAs proximity cap to prevent As outdiffusion. Other details of the sample growth are described in Ref. [30].

The SPV measurements were performed using a contactless electrode configuration with a chopped light in air at room temperature. The light from a 250 W tungsten-halogen lamp was passed through a 0.32 m Jobin-Yvon monochromator, chopped at 180 Hz and focused onto the sample. The sample is mounted in a capacitor like sample holder on a bottom electrode (i.e., a copper plate) and covered by a top electrode (i.e., a metal grid). The induced SPV signal on the metal grid was measured with a copper bottom as the ground electrode, using a buffer circuit and a lock-in amplifier [26].

A "bright configuration" of experimental set-up was used to measure the PR and contactless electroreflectance (CER) spectra [31]. A single grating 0.55 meter focal-length monochromator and a Si *pin* photodiode were used to disperse and detect the reflected light from the samples. A 150 W halogen lamp was used as the probe beam and a YAG laser (532 nm line) was used as the pump source. The probe and pump beams were focused onto the sample to the diameter of ~3 mm and the power of laser beam was reduced to 10 mW using a neutral density filter. The pump beam was modulated by a mechanical chopper at a frequency of 280 Hz. For CER measurements samples were mounted in a capacitor with the top electrode made from a copper-wire mesh which is semi-transparent to light. This electrode was kept at a distance of ~0.5 mm from the sample surface while the sample itself was fixed on the bottom copper electrode. A maximum peak-to-peak alternating voltage of ~3.0 kV with the frequency of 285 Hz was applied. Phase sensitive detection of the PR and CER signals was accomplished using a lock-in amplifier. Other relevant details of CER and PR measurements are described in Refs. [31,32].

3. Results and discussion

Fig. 2 shows room temperature SPV and PR spectra measured for GaAs layer (reference sample) and as-grown and annealed GaNAs

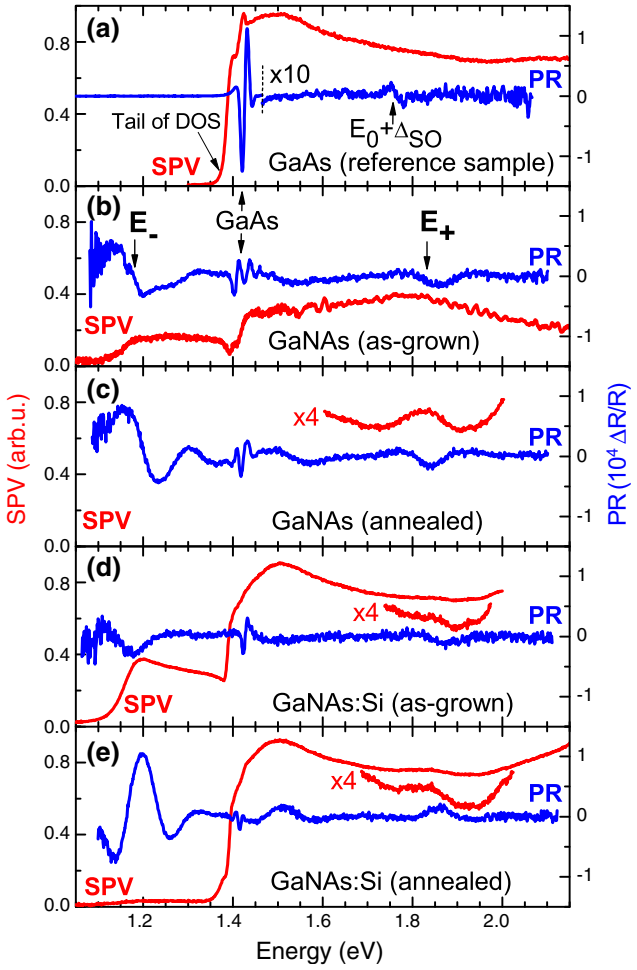

Fig. 2. Room temperature SPV and PR spectra of the reference sample (a), as-grown (b) and annealed $GaN_{0.014}As_{0.986}$ (c) samples, and as-grown (d) and annealed $GaN_{0.0135}As_{0.9865}$:Si (e) samples.