Room-temperature photoresponse of Schottky photodiodes based on GaN_xAs_{1-x} synthesized by ion implantation and pulsed-laser melting

Wei Yi,[a] Taeseok Kim,[b] Ilan Shalish, Marko Loncar, Michael J. Aziz, and Venkatesh Narayanamurti
School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

(Received 31 August 2010; accepted 22 September 2010; published online 11 October 2010)

The spectral responsivity for Schottky photodiodes based on the GaN_xAs_{1-x} alloys synthesized using nitrogen (N) ion implantation followed by pulsed-laser melting and rapid thermal annealing is presented. An N-induced redshift up to 250 meV (180 nm) in the photocurrent onset energy (wavelength) is observed. The N concentration dependence agrees with the values measured by photomodulated reflectance and ballistic electron emission microscopy, and with the calculation by the band anticrossing model for the splitting of the conduction band in GaN_xAs_{1-x}. © *2010 American Institute of Physics*. [doi:10.1063/1.3500981]

Highly mismatched semiconductor alloys (HMAs), compound semiconductors in which a small fraction of the anions is replaced by more electronegative elements, have become important due to their dramatic changes in electronic properties from the host materials and motivated many potential technological applications.[1] GaN_xAs_{1-x} is a HMA known especially for its large band gap reduction of as much as 180 meV per $x=0.01$ up to a few percent.[2,3] Ion implantation (II) followed by a combination of pulsed laser melting (PLM) and rapid thermal annealing (RTA), a highly nonequilibrium route utilizing energetic ion and photon beams, has recently been shown to produce high quality thin films of GaN_xAs_{1-x}.[4,5] The extremely fast (<100 ns) melting and solidification rates in the PLM process result in highly supersaturated substitutional solid solutions[6] giving rise to a large band gap reduction comparable to that of alloys grown by conventional thin film growth methods.

We have recently demonstrated two dimensionally (2D) patterned GaN_xAs_{1-x} nanostructures synthesized by patterned II followed by unpatterned transient thermal processing, which holds potential for lateral control of the conduction band edge, thereby enabling the development of a variety of 2D quantum devices from HMAs.[7,8] A combination of ballistic electron emission microscopy (BEEM) and photomodulated reflectance (PR) spectroscopy was used to systemically investigate the effects of the incorporated N concentrations on the band structure of the GaN_xAs_{1-x} alloy. We have shown that the band gap of such synthesized GaN_xAs_{1-x} nanodots can be tuned from 866 nm all the way up to 1100 nm, thus extending the wavelength range of GaAs based photodetectors. However, there is so far no experimental demonstration of optoelectronic devices utilizing HMAs with engineered band gaps and carrier confinements.

To demonstrate steered photoresponsivity of HMAs, we aimed at synthesizing GaN_xAs_{1-x} based one-dimensional confined quantum well structure using blanket II-PLM-RTA. In this paper, we fabricated GaN_xAs_{1-x} based Schottky photodetectors and characterized their performance using photocurrent (PC) spectroscopy. We demonstrate that it is feasible to utilize II-PLM-RTA fabricated GaN_xAs_{1-x} materials for near infrared photodetectors, whose spectral response can be precisely controlled by controlling the N content.

A 100 nm unintentionally doped GaAs layer was grown on a (001)-oriented n^+ GaAs substrate. Table I summarizes the processed samples used in the present study. For sample R, A, P, B, and C, nitrogen ions (N^+) were blanket implanted by using an ion energy of 15 keV with different doses from 0.3×10^{15} to $3.2\times10^{15}/cm^2$. The GaAs regions were implanted down to ~80 nm depth with N atomic concentration from 4.9×10^{19} to $4.0\times10^{20}/cm^3$ at the peak of the distribution. The GaAs samples were then pulsed laser melted in air using a XeCl excimer laser ($\lambda=308$ nm) with a pulse duration of ~30 ns full width at half maximum. Through a multiprism beam homogenizer, the laser formed a uniform rectangular shaped spot with less than 4% rms intensity variation. The melt durations were determined by measuring the time resolved reflectivity of the samples using a low-power continuous-wave argon-ion ($\lambda=488$ nm) probe laser. The excimer laser fluence for all the samples is 0.25 J/cm^2 and the as-implanted amorphized thickness was estimated to be 80 nm from the implantation profile calculation. Further details on the PLM process can be found in Ref. 8. All of the N implanted samples, plus a witness sample S without N implantation, were treated by RTA after PLM at 950 °C for 5 s in flowing N_2, as reported in a previous study.[4] Figure 1 shows the secondary ion mass spectroscopy (SIMS) N depth profiles, which indicate that N redistribution has occurred following PLM and RTA. N concentration is peaked at

TABLE I. Summary of II-PLM-RTA treated GaN_xAs_{1-x} samples.

Sample ID	N dose (10^{15} cm^{-2})	N_p [a] (10^{20} cm^{-3})	x_p [b]
S	0.0	...	...
R	0.3	0.5	0.0022
A	1.2	1.5	0.0068
P	1.8	2.9	0.0131
B	2.5	3.7	0.0165
C	3.2	4.0	0.0181

[a]Peak N concentration measured by SIMS after II-PLM-RTA.
[b]Peak anion sublattice occupation fraction after II-PLM-RTA.

[a]Present address: Information and Quantum Systems Lab, Hewlett-Packard Laboratories, Palo Alto, California 94304, USA. Electronic mail: weiyi@seas.harvard.edu.
[b]Present address: SunPower Corporation, San Jose, California 95134, USA.

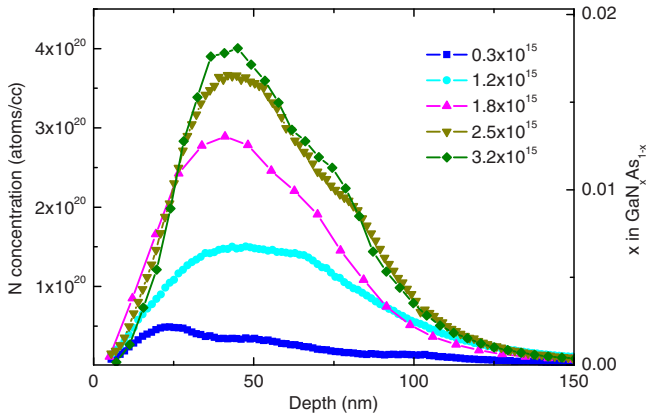

FIG. 1. (Color online) SIMS depth profile of nitrogen concentration for GaAs samples treated with II-PLM-RTA. Labels show the nitrogen doses in atoms per centimeter square implanted at 15 keV. The PLM was performed at 0.25 J/cm^2 laser fluence. All the samples were treated by RTA at 950 °C for 5 s in 1 atm of N_2.

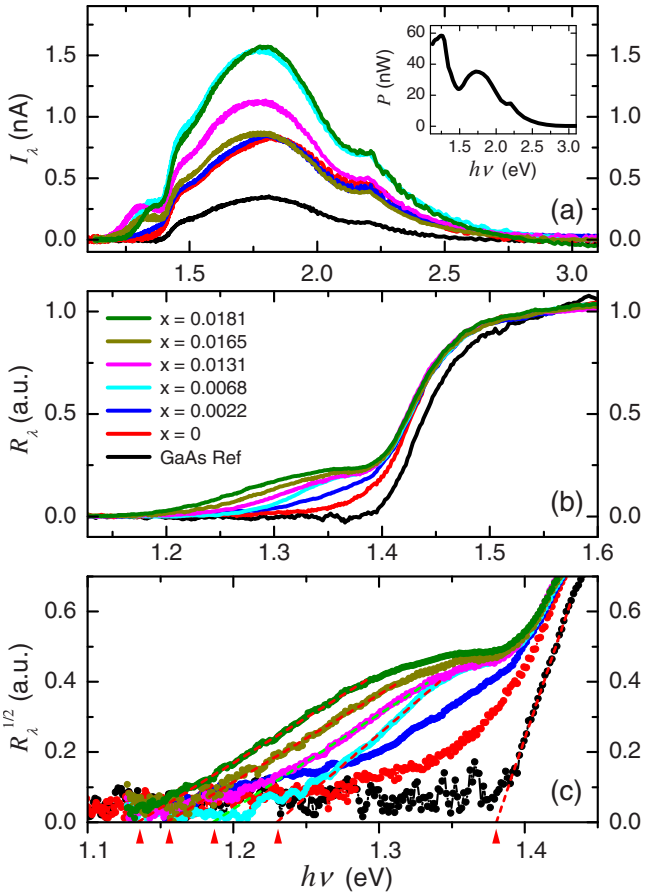

FIG. 2. (Color online) (a) PC of GaN_xAs_{1-x} based Schottky diodes. Inset shows the illumination power measured with a calibrated Si detector and a power meter. (b) Responsivity of the same samples calculated by dividing the PC by the illumination power. All the curves are normalized by the corresponding values at 800 nm for clarity. (c) Square root of the responsivity. Dashed lines are linear fits. Arrows indicate the responsivity turn-on thresholds.

~40 nm depth, except for sample R with lowest N^+ dosage peaked at ~24 nm. Although some tailing of N^+ concentration into the n-GaAs substrate is evident, most of the implanted N^+ are constrained in the 100 nm undoped epilayer (80%–90% by integrating the curve area).

To fabricate Schottky photodiodes, nonalloyed Ni/Ge/Au Ohmic contacts were first deposited by e-beam evaporation onto the bottom of the n^+ GaAs substrates. To avoid any possible change of the N treated region, no postdeposition annealing was performed. For Schottky contacts, Au base films of 8 nm thickness patterned by photolithography were deposited on the undoped GaAs surface by thermal evaporation at a typical pressure 5×10^{-7} torr. Immediately prior to Au evaporation, the GaAs surfaces were treated in a 1:10 solution of $NH_4OH:H_2O$ for 60 s followed by a few seconds of deionized water rinse and nitrogen gas blow dry. The effective area of the device was 0.24 mm^2 (400×600 μm). As a reference, Schottky diodes made from the same GaAs epiwafer without treatment by N II-PLM-RTA were also fabricated and tested. For PC spectroscopy measurements, the diode current was measured under a constant reverse bias of 1 V. The top surface of the Au base contact was illuminated with a focused beam of monochromatic light scanned from 1100 to 400 nm with 1 nm steps. The monochromatic light was supplied from a Gemini 180 double monochromator (Jobin Yvon, Ltd.) with 0.18 m focal length and 0.15 nm resolution using a 250 W tungsten halogen lamp as the light source. Incident light was coupled through a multimode fiber and focused through a lens pair onto the effective area of each device. All the measurements were performed in air at room temperature.

Figure 2(a) shows typical traces of PC (I_λ) versus photon energy $h\nu$ after subtracting the dark current (typically less than a few nanoamperes at reverse bias of 1 V). The spectral dependence of the illumination power P [see Fig. 2(a) inset] was measured by a calibrated silicon photodiode and an optical power meter, which maximized at 1.255 eV (wavelength $\lambda=988$ nm). Photoresponsivity $R_\lambda \propto I_\lambda/P$ is therefore deduced. Note that no attempt was made to acquire the absolute responsivity or quantum efficiency due to the lack of a calibrated blackbody source. However, for the present work we are mostly interested in the spectral dependence of R_λ instead of its absolute value. Figure 2(b) shows the responsivity spectra for all the samples. For easier comparison, all the curves are normalized by the corresponding values at 1.55 eV ($\lambda=800$ nm). Compared with the GaAs reference which shows a responsivity cutoff near ~1.4 eV, N implanted samples exhibit a shoulder structure below the GaAs absorption edge. The onset of the responsivity can be determined after replotting the same set of data as $R_\lambda^{1/2}$ versus photon energy, as shown in Fig. 2(c). According to Fowler's relation, $R_\lambda^{1/2}$ should show a linear energy dependence in the near-threshold regime.[9] An exception is found for sample S and R treated with zero or low N dosage, in which R_λ gradually tails off instead of showing a clear onset threshold. A linear fit of $R_\lambda^{1/2}$ was used to obtain the responsivity onset thresholds. The PC onset thresholds [indicated by the arrows in Fig. 3(c)] shift to lower energies as N concentration increases. For sample C with the largest N peak concentration of $x=0.0181$, the PC onset threshold is 246 meV lower than that of the GaAs reference sample. Note that for the GaAs reference sample, the fitted onset threshold at 1.381 eV is 43 meV lower than the GaAs band gap of 1.424 eV. As shown later, the band gaps of GaN_xAs_{1-x} alloys can be derived after taking this systematic underestimate into account.

It is noteworthy that in our PC measurements, excitation light is a weak perturbation and excess diode current appears once quasithermal equilibrium electron-hole pairs are gener-

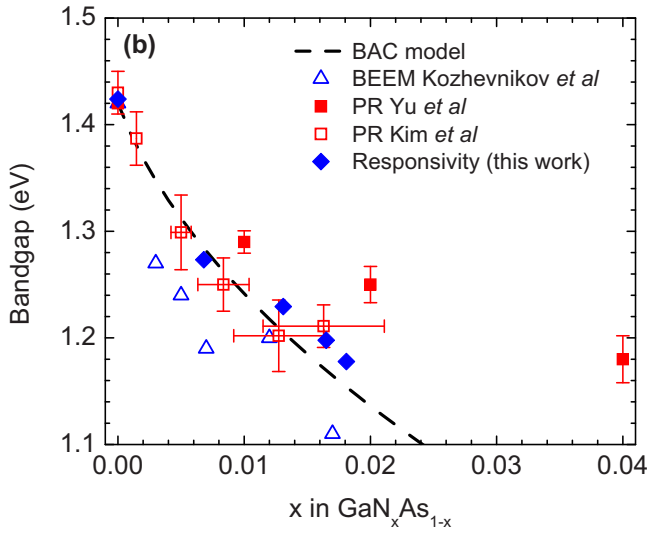

FIG. 3. (Color online) Band gap energies of GaN_xAs_{1-x} vs N concentration from the fitting of responsivity spectra (diamonds) compared with results of PR from Refs. 5 and 8 (squares), and values deduced from BEEM (Ref. 10) (triangles). The dashed line is the calculated values from the BAC model.

ated across the forbidden gap, i.e., where there is a conduction band minimum produced by the peak N concentration. The onset energy in PC can therefore be attributed to the band gap of GaN_xAs_{1-x}. As indicated by the PC onset energies, the band gaps between the valence band maximum and the lower conduction subband E_- of the synthesized GaN_xAs_{1-x} layer are observed at energies lower than the band gap of GaAs measured on the unimplanted sample. In Fig. 3, the fitted band gap energies for the GaN_xAs_{1-x} layer are plotted versus N concentration. Note that a 43 meV adjustment was added to the fitted values determined from the GaAs reference sample. The dashed line represents the E_- conduction subband in the band anticrossing (BAC) model,[11,12] which is given by

$$E_{\pm}(k) = \tfrac{1}{2}\{E_N + E_M(k) \pm \sqrt{[E_N - E_M(k)]^2 + 4C_{NM}^2 x}\},$$

where E_N is the energy of the N level, $E_M(k)$ is the dispersion relation for the host matrix, and C_{NM} is the matrix element for the coupling between N states and the extended states. Here, we used the GaN_xAs_{1-x} parameter values of $E_N = 1.65$ eV, $E_M = 1.43$ eV, and $C_{NM} = 2.7$ eV as established previously to fit the experimental data.[12] Notice that the nitrogen concentrations for the abscissa are determined differently in previous studies, by the measured N mole-fractions in the deposited alloy,[10] or corresponding x values in the BAC equation for the measured E_-,[5] or the averaged N concentration over the estimated maximum melting depth.[8] In the present study, we used the N peak concentrations from the SIMS profile to plot the E_- determined by the PC onset thresholds, which match the PR plot from Ref. 8. This is reasonable, because for a GaN_xAs_{1-x} alloy with a nonuniform nitrogen concentration profile, the PC threshold values tend to be more sensitive to the lowest band gap region; whereas in PR measurements the model fitting has been known to collectively reflect the graded band-gap structure.[13]

To summarize, we have demonstrated engineered near-infrared photoresponse of Schottky photodiodes based on HMA GaN_xAs_{1-x}, synthesized using N ion implantation followed by pulsed-laser melting and RTA. We succeeded in redshifting the GaAs responsivity onset by 250 meV to ~1.18 eV (from 870 to 1050 nm), showing the potential of developing optoelectronic devices via synthesis routes based on energetic ion and photon beams.

This work was supported by a DARPA HUNT Contract No. 222891-01 sub-award from the University of Illinois at Urbana-Champaign and by the National Science Foundation under Grant No. NSF-ECCS-0701417. The support of the Center for Nanoscale Systems (CNS) at Harvard University is also acknowledged. We also thank Kin Man Yu at Lawrence Berkeley National Laboratory for supporting the RTA processing of samples.

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