Probing the electronic structures of III–V-nitride semiconductors by x-ray photoelectron spectroscopy

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The electronic structures of III–V-nitride semiconductors, including InGaAsN, GaAsN, and InAsN grown by molecular beam epitaxy, were investigated by high-resolution x-ray photoelectron spectroscopy using synchrotron radiation beam and low energy Ar⁺ sputtering. The N(1s) core-level photoelectron spectra show a single peak with a binding energy (E_b) $\sim$ 398.0 eV of N–Ga bonding for GaAsN sample. For the InAsN samples, a single N(1s) peak at $E_b \sim$ 397.0 eV of N–In bonding is observed. For the InGaAsN samples, the N(1s) spectra exhibit two peaks with a major component corresponding to N–In bonding, and a minor one to N–Ga bonding. The integrated N(1s) intensity of N–In bonding has a higher value than that of N–Ga bonding, in spite of the lower mole fraction of In for the InGaAsN sample. The data indicate that N has a bonding configuration with In-rich nearest neighbors in the InGaAsN samples. © 2004 American Vacuum Society. [DOI: 10.1116/1.1735802]

I. INTRODUCTION

The epistuctures of dilute III–V nitrides on GaAs provide an alternative material to InGaAsP/InP for photonic devices for fiber communications in the $\lambda = 1.3$ – $1.6 \mu\text{m}$ region.^{1,2} Molecular beam epitaxy (MBE) and metal-organic chemical-vapor deposition (MOCVD) have been widely used to prepare InGaAsN structures.^{3,4} Recently, high quality diode laser performance, such as $\lambda = 1.3 \mu\text{m}$ edge-emitting lasers and vertical cavity surface emitting lasers (VCSELs), have been demonstrated.^{5,6} Further understanding of the InGaAsN microscopic properties will facilitate band gap engineering and device fabrication. The incorporation of N, which has a much larger electronegativity and smaller atomic size compared to As, makes the InGaAsN electronic structure and its relation to band gap properties an interesting topic to investigate. The nearest-neighbor bonding configuration of the isovalent nitrogen in InGaAsN, i.e., In–N or Ga–N rich, has a strong influence on the band gap.^{7,8} Recently, Kim and Zunger⁹ studied the N bonding distribution for the equimolar In_{0.5}Ga_{0.5}As_{0.5}N_{0.5} system by using Monte Carlo (MC) simulation to calculate the “short range order” (SRO) parameter decided by strain and cohesive energy. Their results show that N is surrounded in a preferred In-rich nearest-neighbor configuration for this alloy. X-ray photoelectron spectroscopy (XPS), which directly probes the core-level photoelectron signal, provides an efficient method to explore the nearest-neighbor bonding configuration for N.

However, the very dilute N mole fraction and surface oxidation make the N(1s) spectra measurement much more difficult.¹⁰ In this article, we are able to observe the N(1s) signal of the MBE-grown InGaAsN, GaAsN, and InAsN by using a high-resolution synchrotron radiation light and low-energy Ar⁺ sputtering. The XPS data of GaN, InN, InGaAs, and GaAs have also been measured for reference. The XPS data exhibit a stronger N(1s) signal intensity for N–In bonding than N–Ga bonding in the InGaAsN samples with and without post-growth annealing. This result indicates that N–In is the dominant bonding configuration in the InGaAsN samples prepared by MBE.

II. EXPERIMENT

The III–V-nitride samples included in this study are the following: (1) In_{0.38}Ga_{0.62}AsN/GaAs quantum well structure (TR577) grown by solid source MBE with a N₂ plasma source. The 60 Å-thick In_{0.38}Ga_{0.62}AsN layer of 5% N mole fraction was grown at 400 °C on the GaAs buffer layer, and a 3000-Å-thick GaAs cap layer was grown at 600 °C on top of the In_{0.38}Ga_{0.62}AsN layer. Therefore, the In_{0.38}Ga_{0.62}AsN layer was under annealing during the growth of the GaAs cap layer. (2) GaAsN/GaAs structures of 2% (TR595) and 2.3% N mole fraction (TR617), respectively, were grown by solid source MBE with a N₂ plasma source. The growth temperature was 450 °C, and the thickness of the GaAsN layers was 2000 Å. (3) In_{0.53}Ga_{0.47}AsN/InP structure (C1024) of 2.8% N mole fraction was grown at 400 °C on the InP substrate by gas source MBE with a N₂ plasma source. The thickness of the In_{0.53}Ga_{0.47}AsN film is about 3000 Å. A piece of the

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wafer, denoted by C1204a, was subjected to post-growth annealing. The annealing condition was at 575 °C and 5 min in a N₂ atmosphere. (4) InAsN/InP structures of 10% (C1396) and 4.2% N mole fraction (C1413), respectively, were grown at 450 °C on the InP substrate by gas source MBE with a N₂ plasma source. In addition to the above samples, we have also performed the XPS measurement on InN, GaN, GaAs, and InGaAs as reference samples.

The high-resolution XPS measurement was carried out at the U5 beamline of National Synchrotron Radiation Research Center, Taiwan (NSRRC). The sample was clamped on a tantalum plate in an UHV ($\sim 10^{-10}$ Torr) chamber equipped with a VG CLAM II electron-energy analyzer. The incident angle of photons was 55° from the surface normal, and the emitted photoelectrons were collected with the analyzer normal to the sample surface. The combined resolution of the monochromator and analyzer is about 0.1 eV. An Ar⁺ sputtering gun is installed to facilitate the *in situ* depth-profile measurements. The sample surface was sputter cleaned by Ar⁺ at energy ≤ 1.5 keV, and a beam current density of $\sim 0.1 \mu\text{Acm}^{-2}$ with an argon partial pressure of $\sim 1 \times 10^{-6}$ Torr. The conditions were chosen to minimize preferential sputtering and surface damage. The sample charging effect could cause an energy shift in the XPS. To carefully calibrate the energy shift originated from the compositional variations of the different samples, an Au foil was attached to the sample holder and the Au Fermi level was measured as energy reference for each sample. The binding energies in the collected spectra were then obtained by comparing the observed C(1s)- and/or O(1s)-to-Au Fermi level energy separations to the standard values.

III. RESULTS AND DISCUSSION

The samples were first cleaned by Ar⁺ sputtering in the XPS chamber, and the full range spectra, including O(1s), As(3d), In(3d), and Ga(3d), were measured to make sure of the removal of surface contamination and oxidation. Figures 1(a) and 1(b) show the N(1s) spectra of GaAsN samples, TR595 (N=2%) and TR617 (N=2.3%), respectively, measured at photon energy $h\nu=600$ eV. Both of the samples show a clear N(1s) peak at $E_b \sim 398.0$ eV, and the data ensure the high XPS sensitivity by the synchrotron radiation. The N(1s) signal from GaAsN is compared to the signal from GaN, as shown in Fig. 1(c). The peak intensity of the N(1s) from GaN is more than 50 times higher than the signal from GaAsN samples. The N(1s) signals for the three samples all originated from N–Ga bonding at $E_b \sim 398.0$ eV. For the N–In bonding, we have examined the InAsN and InN samples, as shown in Fig. 2. The spectra show a more serious surface oxidation, and a weak N(1s) component of N–O bonding at $E_b \sim 399.3$ eV both in InN and InAsN samples after sputtering. However, in Figs. 2(a)–2(c), a prominent N(1s) peak consistently appears at $E_b \sim 397.0$ eV, which corresponds to the N(1s) core-level photoelectrons of N–In bonding. From the data shown in Figs. 1 and 2, the N(1s) photoelectron spectra of dilute GaAsN and InAsN samples were obtained. We have identified the N(1s)

FIG. 1. (a) and (b) N(1s) photoelectron spectra for the GaAsN samples. (c) N(1s) XPS data for GaN. The E_b is ~ 398.0 eV for N(1s) of N–Ga bonding.

binding energies at $E_b \sim 398.0$ eV for N–Ga bonding configuration (i.e., 4-Ga nearest neighbors), and $E_b \sim 397.0$ eV for N–In bonding configuration (4-In nearest neighbors), respectively.

As for the InGaAsN sample, the depth profile of XPS data is illustrated in Figs. 3(a)–3(d) for the InGaAsN/GaAs QW structure (TR577, N=5%). Before the TR577 sample was loaded into the XPS chamber, the GaAs cap layer was wet etched to ~ 500 Å to shorten the Ar⁺ sputtering procedure and to avoid possible surface damage. At the very beginning of the experiment, the N(1s) XPS data show a strong signal near $E_b \sim 399.3$ eV, as shown in Fig. 3(a), possibly of N–O bonding induced by chemical etching on the GaAs cap layer.

FIG. 2. (a) N(1s) photoelectron spectrum for InN. (b) and (c) N(1s) XPS data for InAsN samples. The E_b is ~ 397.0 eV for N(1s) of N–In bonding.

FIG. 3. Depth profile of the N(1s) photoelectron spectra for the $\text{In}_{0.38}\text{Ga}_{0.62}\text{AsN}/\text{GaAs}$ quantum well sample. From (a)–(d) are the traces as the sputter-exposed surface approaches the InGaAsN layer.

As the sputter-exposed surface approaches the InGaAsN quantum well, the N(1s) signal becomes much weaker, and the main peak shifts to lower binding energy, as shown in Figs. 3(b)–3(d). The spectra have been curve fitted and deconvoluted into three Voigt shapes with peaks at $E_b \sim 397.0$, 398.0 , and 399.3 eV, corresponding to the N–In, N–Ga, and N–O bondings, respectively. Here, we note that ideally N has five different nearest-neighbor configurations for InGaAsN, and their binding energies are closely distributed in the interval of 1 eV (i.e., 397.0 eV of 4-In configu-

TABLE I. Binding energies of N(1s) and the chemical bondings for the III–V-nitride samples.

E_b of N(1s)	Bonding	Samples
397.0 eV	N–In	InN, InAsN, InGaAsN
398.0 eV	N–Ga	GaN, GaAsN, InGaAsN
399.3 eV	N–O	InN, InAsN, InGaAsN

ration to 398.0 eV of 4-Ga configuration).^{10,11} Therefore, the curve fitting, limited by the instrument resolution and the finite full width at half maximum (FWHM) of the spectra, was practical by only considering the 4-Ga and 4-In configurations. We have also measured the InGaAsN/InP samples (C1204 and C1204a) grown by gas source MBE, and summarized all the N(1s) spectra of the III–V nitrides in Fig. 4. For the InGaAsN/InP samples, the N(1s) have a broader spectrum and a main peak near $E_b \sim 397.0$ eV, as shown in Figs. 4(e) and 4(f), similar to the InGaAsN/GaAs data [TR577 in Fig. 4(d)]. After carefully fitting the spectra in Fig. 4, the N(1s) spectra of all the InGaAsN samples show a major peak at $E_b \sim 397.0$ eV, and a minor peak at $E_b \sim 398.0$ eV, consistent with the N–In signal from InAsN, and the N–Ga signal from GaAsN, respectively. The binding energies of N(1s) and the chemical bondings for the III–V-nitride samples are summarized in Table I.

The Ga(3d) spectra have also been investigated for the Ga-related III–V nitrides. The Ga(3d) signals are summarized and compared with the data from InGaAs, GaAs, and GaN, as shown in Fig. 5. The binding energies of Ga(3d) for Ga–As and Ga–N bondings are observed at $E_b \sim 19.5$, and 20.7 eV, respectively, from the GaAs and GaN samples in Figs. 5(g) and 5(h). For the GaAsN samples [Figs. 5(e) and 5(f)], the Ga(3d) signal has a clean peak at $E_b \sim 19.5$ eV,

FIG. 4. N(1s) photoelectron spectra of (a) InN, (b) and (c) InAsN (C1396 and C1413), (d), (e), and (f) InGaAsN (TR577, C1204, and C1204a), (g) and (h) GaAsN (TR595 and TR617), and (i) GaN, respectively. The N(1s) signal of N–In bonding has a stronger intensity than that of N–Ga bonding in the three InGaAsN samples.

FIG. 5. Ga(3d) photoelectron spectra of (a) InGaAs, (b), (c), and (d) InGaAsN (TR577, C1204, and C1204a), (e) and (f) GaAsN (TR595 and TR617), (g) GaAs, and (h) GaN, respectively. (a)–(d) also show the In(4d) spectra of the $4d_{5/2}$ and $4d_{3/2}$ components.

TABLE II. XPS signal intensity ratio of N(1s) from N–In and N–Ga bondings for the three InGaAsN samples.

Sample No.	N–In/N–Ga	
	XPS signal intensity ratio	Effective ratio for In _{0.5} Ga _{0.5} AsN
C1204, In _{0.53} Ga _{0.47} AsN	3.8	3.4
C1204a, In _{0.53} Ga _{0.47} AsN	2.5	2.2
TR577, In _{0.38} Ga _{0.62} AsN	1.5	2.4

which is consistent with the Ga(3d) signal from Ga–As bonding, and no signal of Ga–N has been observed. In the InGaAsN samples in Figs. 5(b)–5(d), the spectra spanning from $E_b \sim 17$ to 20 eV can be decomposed into the signals from Ga(3d) and In(4d) photoelectrons. The result is consistent with the spectrum measured from InGaAs sample, as shown in Fig. 5(a). For the C1204, and C1204a samples, a very weak component appears at E_b higher than 21 eV, which is attributed to intermediary Ga oxidation states.¹²

To quantitatively analyze the N bonding distribution in InGaAsN, we have integrated the areal intensity of N(1s) XPS signals from N–In, and N–Ga bondings, respectively. The ratio of the XPS areal intensity of N(1s) for N–In and N–Ga is listed in Table II for the three InGaAsN samples. For all three samples, the N–In/N–Ga ratio is always larger than one. It means that, even in the TR577 sample of higher mole fraction of Ga, the N prefers to be seated in an In-rich environment. We have taken into account the mole fraction ratio of In and Ga in the InGaAsN compounds, and weighted it to the values of N–In/N–Ga. Here, we note that the values of In and Ga mole fraction were obtained from the MBE growth conditions. The effective ratio for the N–In and N–Ga bonding distribution can be obtained for the case of In_{0.5}Ga_{0.5}AsN compounds. The effective ratio of N–In/N–Ga is ~ 3.4 for the In_{0.53}Ga_{0.47}AsN (C1204) without annealing. For the annealed samples, C1204a and TR577, the effective N–In/N–Ga ratio is 2.2, and 2.4, respectively. This result is in good agreement with the prediction of the dominant presence of N-centered In₃Ga₁ clusters in the annealed InGaAsN samples.^{7,9}

IV. CONCLUSION

The N(1s) photoelectron signals of dilute III–V nitrides have been observed by using high-resolution synchrotron radiation light source and low-energy Ar⁺ sputtering. The XPS data were measured from the MBE-grown InGaAsN, GaAsN, and InAsN samples. The N(1s) peak is located at

$E_b \sim 397.0$ eV for InAsN and InN samples. For GaAsN, the N(1s) peak is at $E_b \sim 398.0$ eV consistent with the one observed in GaN. As for the InGaAsN samples, the N(1s) signal shows a major peak corresponding to In–N bonding, and a minor component of Ga–N bonding. The integrated N(1s) intensity of N–In bonding has a higher value than that of N–Ga bonding despite the lower mole fraction of In for the InGaAsN sample. The data suggest that the MBE-grown InGaAsN has an In–N rich bonding configuration.

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