Direct observation of N-(group V) bonding defects in dilute nitride semiconductors using hard x-ray photoelectron spectroscopy

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(Received 23 February 2011; accepted 13 March 2011; published online 25 March 2011)

Using bulk sensitive hard x-ray photoelectron spectroscopy, we directly observe a spectrum related to N–As bonding defects in (Ga,In)(N,As)/Ga(N,As) heterostructure. The defects are most likely attributed to split interstitials. Their concentration is in the order of 10^{19} cm^{-3}, close to the detection limit of the measurement. Rapid thermal annealing eliminates the defects, leading to those undetectable. Similar phenomenon is observed for N–P bonding defects in In(N,P). The results indicate common features in dilute nitride semiconductor system: existence of N-(group V) bonding defects and their behavior on postgrowth annealing. © *2011 American Institute of Physics*. [doi:10.1063/1.3573789]

Dilute nitride semiconductors are material systems of interest because of their tunability of band gap, showing prospects for the next generation optical devices operating at the wavelengths previously unachievable.[1–3] Due to the requirement of low growth temperature, the as-grown samples of dilute nitrides are known to contain a quantity of defects within the crystal, such as interstitials,[4,5] antisites,[6] and vacancies.[7] The reduction in the defects is generally required to improve the optical and electrical characteristics of the materials. Therefore, postgrowth annealing is a vital technique for its application to devices.[4] Meanwhile, due to the unique properties of the defects themselves, an active utilization of those can realize advanced functional devices such as a spin-filter operating at room temperature.[5] Hence, the characterization of the defects, and the control of their amount by annealing, have been studied over the past decades.[4,8] X-ray photoemission spectroscopy is widely employed for the investigation of the electronic structures of matters, including the defects in dilute nitride system.[9,10] Using standard Al or Mg anodes having its x-ray energy about 1 keV, the escape depth of the photoelectrons is several nano meters. Then, the signal is strongly affected by the surface condition as well as the out-diffusion of the elements especially at the case after annealing.[10] Besides, high photon flux realized by the undulators at third-generation synchrotron light sources and the development of the electron energy analyzer for high kinetic energy electrons have recently made the high-resolution hard x-ray photoelectron spectroscopy (HXPES) practically available. The larger escape depth of photoelectrons as deep as several-tens nanometer with higher kinetic energy will facilitate nondestructive studies of bulk materials, nanoscale buried layers and their interfaces.[11,12] In this report, we show the defect characteristics of a dilute nitride (Ga,In)(N,As) and In(N,P) proved by HXPES. The bonding-configuration of the observed defects is identified, and their behavior on the postgrowth annealing is investigated.

We investigate two dilute nitride samples: a (Ga,In)(N,As) sample grown on GaAs substrate and an In(N,P) sample grown on InP substrate. The samples were grown by molecular beam epitaxy at a carefully optimized conditions for each materials to contain large amount of nitrogen preserving ideal structural properties. Details of the growth and the properties of the samples can be found in Refs. 13 and 14. The (Ga,In)(N,As) sample consists of ten periods of [(Ga,In)(N,As) (7 nm)/ Ga(N,As) (14 nm)] with constituents' compositions of 36% In and 4.5% N for the (Ga,In)(N,As) wells and 0.8% N for the Ga(N,As) barriers. Note that the top layer of the sample is Ga(N,As) as shown in Fig. 1. The In(N,P) have its thickness of 100 nm with N concentration of 0.5% existing at the top of the sample. To investigate the effect of annealing, rapid thermal annealing (RTA) is conducted for 1 min. under N_2 ambient at 700 °C after the growth. The condition was employed to appropriately enhance the luminescence efficiency of the samples.[13,14] During the RTA, the samples were proximity-capped with a GaAs wafer to prevent the evaporation of constituent elements. The HXPES measurement was carried out at BL46XU beamline of SPring-8.[11,12] The undulator x-ray was monochromatized by the Si (111) double crystal monochromator and was further monochromatized by a Si (111) channel cut postmonochromator. The photon energy was set to 7.94 keV using Si (444) reflections of the postmonochromator. For the photoelectron energy analysis, VG-SCIENTA R-4000 was used, and the pass-energy was set to 200 eV. The incident x-ray angle and the photoelectron take-off-angle with respect to sample surface were 10° and 80°, respectively. The detection limit of the measurement was roughly estimated to be 2×10^{19} cm^{-3}.[15] The binding energy was calibrated with the $4f$ core level energy observed from Au thin film directly deposited on the sample surface. For a plain qualitative analysis, observed peak intensity was normalized before and after RTA adjusting the spectral intensities rela-

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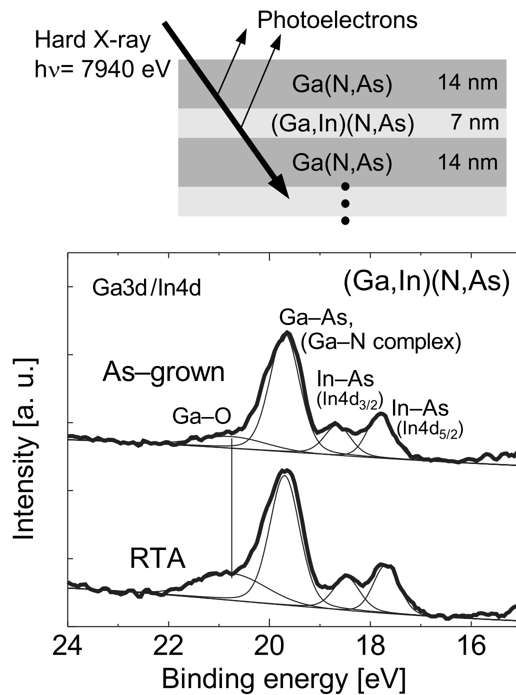

FIG. 1. HXPES spectra of the Ga $3d$ and In $4d$ spectral regions for (Ga,In)(N,As) sample before and after RTA. The condition close to the surface is schematically illustrated.

tive to the peak intensities of dominant group-V elements: As $2p_{3/2}$ peak for (Ga,In)(N,As) sample and P $1s$ peak for In(N,P) sample. Superposed peaks spectrum was deconvoluted by curve fitting using a sum function of Gaussian and Lorentzian profile with its Gaussian percentage about 80%. No special surface cleaning was carried out before the HXPES measurement to access the bare characteristics of the samples.

Figure 1 shows the HXPES spectra of (Ga,In)(N,As) sample at the spectral regions of Ga $3d$–In $4d$ with a schematically illustrated surface condition of the sample. The peaks at 17.8 eV, 18.6 eV, 19.7 eV, and 20.8 eV can be assigned to In–As (In $4d_{5/2}$), In–As (In $4d_{3/2}$), Ga–As (Ga $3d$), Ga–O (Ga $3d$), respectively.[16,17] The distinct peak intensities of the In-related peaks indicate that the probing depth of this measurement is enough to analyze the buried (Ga,In)(N,As) layer below the 14-nm-thick surface Ga(N,As). Before and after RTA, the intensities of Ga and In -related peaks shows negligible difference. The experiment is thus carried out without suffered from In out diffusion, which occurs if the In-containing (Ga,In)(N,As) layer exist close to the surface.[10] Besides, we observe a increase in Ga–O peak intensity after RTA. That indicates the RTA enhances the surface oxidation, induced by the residual oxygen within the RTA furnace or by the native oxide of the GaAs wafer employed for the proximity cap during RTA.

Figure 2 shows the HXPES spectra of (Ga,In)(N,As) sample at O $1s$ region. Each spectrum has at least two components. One originates from atmospheric H–O bonding commonly observed at the surfaces of matters.[18] The other peak at 531.7 eV should be the superposition of oxides of the constituents, namely, dominant component which comes from Ga–O configuration[17,19] with the mixture of the minor components comes from In–O (Ref. 20) and As–O (Ref. 21) configurations. RTA induces the enhancement of the peak

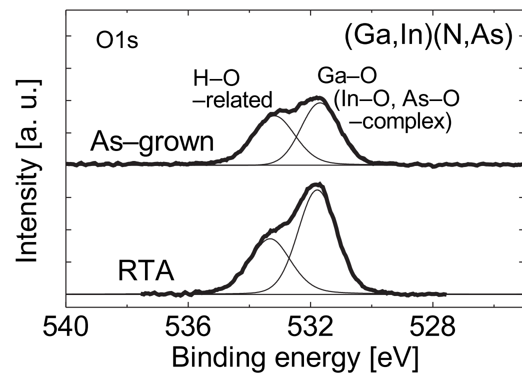

FIG. 2. HXPES spectra of the O $1s$ spectral regions for (Ga,In)(N,As) sample before and after RTA.

intensity of the constituents' oxides. That suggests an increased oxide formation close to the surface as also observed in Fig. 1.

Figure 3 shows HXPES spectra around the energy of As $2p$ before and after RTA. At as-grown condition, we observe a main Ga–As peak at 1323.2 eV with a small subpeak at around 1327 eV.[18] The subpeak can stem from As–O (Ref. 18) or N–As configuration.[22,23] Specifically, the subpeak is vanished after RTA. Considering the surface oxidation discussed in the previous paragraph, the decrease in oxides is unlikely to occur. Consequently, the subpeak is related to N–As configurations. The N–As bonding is itself a defect, which most likely originates from the split interstitial consisting of a nitrogen and an arsenic atom on a single arsenic lattice site.[24,25] The split interstitial defects have been theoretically predicted as a defect having energetically favorable configurations,[24,25] supported with experimental suggestions.[26–29] Taking the detection limit of the measurement into account, the as-grown sample would have the defect concentration in the order of 10^{19} cm^{-3}. The RTA diminishes the defects, resulting in their concentration smaller than $\leq 10^{18}$ cm^{-3}. The estimated concentration before and after annealing is in good agreement with nuclear reaction analysis reported by Ahlgren *et al.*[29]

We examine the above descriptions for another dilute nitride system. Figure 4 shows HXPES spectra for the

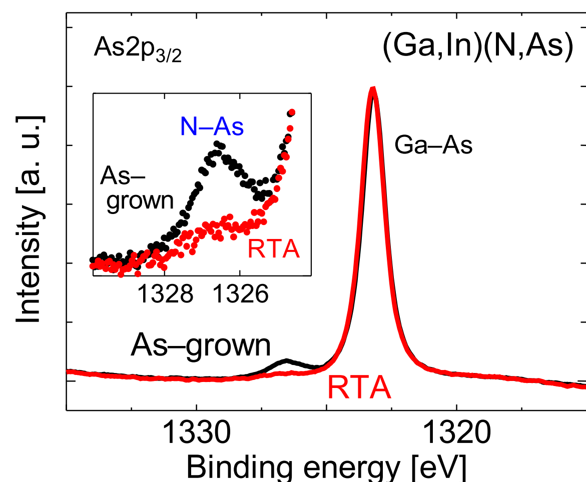

FIG. 3. (Color online) HXPES spectra of the As $2p$ spectral regions for (Ga,In)(N,As) sample before and after RTA. The inset shows the magnified profile for the subpeak around 1327 eV.

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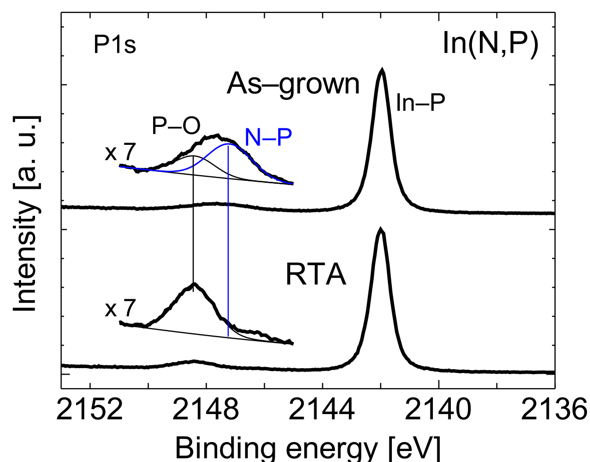

FIG. 4. (Color online) HXPES spectra of the P 1*s* spectral regions for 100-nm-thick In(N,P) sample before and after RTA.

In(N,P) sample at the energy regions of P 1*s*. With the In–P main peak,[30] we observe a peak at around 2148 eV. Comparing the spectra of as-grown and RTA samples, the as-grown sample was decomposed to two peaks with the binding energies of 2148.4 and 2147.2 eV. The 2148.4 eV peak is assigned to be P–O configuration.[30] Then, the peak at 2147.2 eV is expected to be a N–P configuration considering general relationships of the binding energies between nitrides and oxides.[31] The peak intensity is close to the detection limit, suggesting its concentration in the order of 10^{19} cm^{-3}. As also observed for the (Ga,In)(N,As) sample, the N-(P: group V) bonding was vanished after RTA, followed by the increase in the P–O configurations originates from oxides. As discussed in the previous (Ga,In)(N,As) results, the N–P bonding can be identified as N interstitial.

In summary, we have demonstrated that the HXPES can access the bonding configurations of the defects in (Ga,In)(N,As)/Ga(N,As) heterostructure and In(N,P). For both the materials, we directly observed N-(group V) bonding defects within the as-grown crystals having its concentration in the order of 10^{19} cm^{-3} which is close to the detection limit. RTA with proximity cap eliminates the defects, resulting in an undetectable defects density, concomitantly increasing the oxides near the surface.

The HXPES measurements were performed at SPring-8 in cooperation with JASRI through Proposal No. 2008B1926. This work was partly supported by a grant for the Osaka University Global COE Program "Center for Electronic Devices Innovation" and a grant for Scientific Research on Priority Areas from MEXT, Japan and a Grant-in-Aid for Scientific Research (B) from JSPS.

[1]See, e.g., *Dilute Nitride Semiconductors*, edited by M. Henini (Elsevier, Amsterdam, 2005).
[2]N. Tansu, J.-Y. Yeh, and L. J. Mawst, J. Phys.: Condens. Matter **16**, S3277 (2004).
[3]L. J. Mawst, J. Y.-T. Huang, D. P. Xu, J.-Y. Yeh, G. Tsvid, T. F. Kuech, and N. Tansu, IEEE J. Sel. Top. Quantum Electron. **14**, 979 (2008).
[4]S. G. Spruytte, C. W. Coldren, J. S. Harris, W. Wampler, P. Krispin, K. Ploog, and M. C. Larson, J. Appl. Phys. **89**, 4401 (2001).
[5]X. J. Wang, Y. Puttisong, C. W. Tu, A. J. Ptak, V. K. Kalevich, A. Y. Egorov, L. Geelhaar, H. Riechert, W. M. Chen, and I. A. Buyanova, Appl. Phys. Lett. **95**, 241904 (2009).
[6]N. Q. Thinh, I. A. Buyanova, and W. M. Chen, Appl. Phys. Lett. **79**, 3089 (2001).
[7]J. Toivonen, T. Hakkarainen, M. Sopanen, H. Lipsanen, J. Oila, and K. Saarinen, Appl. Phys. Lett. **82**, 40 (2003).
[8]Y. Jin, R. M. Jock, H. Cheng, Y. He, A. M. Mintairov, Y. Wang, C. Kurdak, J. L. Merz, and R. S. Goldman, Appl. Phys. Lett. **95**, 062109 (2009).
[9]T. S. Lay, W. T. Kuo, L. P. Chen, Y. H. Lai, W. H. Hung, J. S. Wang, J. Y. Chi, D. K. Shih, and H. H. Lin, J. Vac. Sci. Technol. B **22**, 1491 (2004).
[10]H. F. Liu, S. Karirinne, C. S. Peng, T. Jouhti, J. Konttinen, and M. Pessa, J. Cryst. Growth **263**, 171 (2004).
[11]K. Kobayashi, Nucl. Instrum. Methods Phys. Res. A **601**, 32 (2009).
[12]H. Yumoto, K. Hirata, A. Nisawa, G. Ueno, M. Sato, J.-Y. Son, T. Koganezawa, M. Machida, T. Muro, I. Hirosawa, M. Suzuki, N. Kawamura, M. Mizumaki, H. Ohashi, M. Yamamoto, Y. Watanabe, and S. Goto, Proc. SPIE **7448**, 74480Z (2009).
[13]F. Ishikawa, M. Höricke, U. Jahn, A. Trampert, and K. H. Ploog, Appl. Phys. Lett. **88**, 191115 (2006).
[14]K. Umeno, Y. Furukawa, N. Urakami, S. Mitsuyoshi, H. Yonezu, A. Wakahara, F. Ishikawa, and M. Kondow, J. Vac. Sci. Technol. B **28**, C3B22 (2010).
[15]M. P. Seah, Vacuum **34**, 463 (1984).
[16]M. Procop, J. Electron Spectrosc. Relat. Phenom. **59**, R1 (1992).
[17]R. Carin, J. P. Deville, and J. Werckmann, Surf. Interface Anal. **16**, 65 (1990).
[18]J. A. Taylor, J. Vac. Sci. Technol. **20**, 751 (1982).
[19]H. Iwakuro, C. Tatsuyama, and S. Ichimura, Jpn. J. Appl. Phys., Part 1. **21**, 94 (1982).
[20]M. Faur, M. Faur, D. T. Jayne, M. Goradia, and C. Goradia, Surf. Interface Anal. **15**, 641 (1990).
[21]D. E. King, J. E. Fernandez, and W. E. Swartz, Appl. Surf. Sci. **45**, 325 (1990).
[22]T. Hashizume, K. Ikeya, M. Mutoh, and H. Hasegawa, Appl. Surf. Sci. **123–124**, 599 (1998).
[23]P. Friedel, J.-P. Landesman, P. Boher, and J. Schneider, J. Vac. Sci. Technol. B **5**, 1129 (1987).
[24]S. B. Zhang and S. H. Wei, Phys. Rev. Lett. **86**, 1789 (2001).
[25]K. Laaksonen, H.-P. Komsa, T. T. Rantala, and R. M. Nieminen, J. Phys.: Condens. Matter **20**, 235231 (2008).
[26]W. J. Fan, S. F. Yoon, T. K. Ng, S. Z. Wang, W. K. Loke, R. Liu, and A. Wee, Appl. Phys. Lett. **80**, 4136 (2002).
[27]W. Li, M. Pessa, and J. Likonen, Appl. Phys. Lett. **78**, 2864 (2001).
[28]M. Reason, H. A. McKay, W. Ye, S. Hanson, R. Goldman, and V. Rotberg, Appl. Phys. Lett. **85**, 1692 (2004).
[29]T. Ahlgren, E. Vainonen-Ahlgren, J. Likonen, W. Li, and M. Pessa, Appl. Phys. Lett. **80**, 2314 (2002).
[30]R. Franke, T. Chassé, P. Streubel, and A. Meisel, J. Electron Spectrosc. Relat. Phenom. **56**, 381 (1991).
[31]M. Losurdo, P. Capezzuto, G. Bruno, G. Leo, and E. A. Irene, J. Vac. Sci. Technol. A **17**, 2194 (1999).

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