Studies of early stages of Mn/GaN(0001) interface formation using surface-sensitive techniques

M. Grodzicki[1*,], P. Mazur[1], A. Krupski[2] and A. Ciszewski[1]**

[1] Institute of Experimental Physics, University of Wrocław, pl. Maksa Borna 9, Wrocław, Poland

[2] Faculty of Science, SEES, University of Portsmouth, Portsmouth, United Kingdom

Abstract

Non-doped GaN(0001) crystals are used as substrates in this study, on which Mn films are vapour deposited in situ under ultrahigh vacuum (UHV). The early stages of the Mn/GaN(0001) interface formation at room temperature are checked out by means of X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and low-energy electron diffraction (LEED). Electron affinity for the already cleaned GaN(0001)-(1×1) surface, achieved by thermal cleaning, is 3.5 eV. The binding energy (BE) of the Ga-3d core level line shifts from 20.3 eV to 19.8 eV and the Mn-3p state from 47.6 eV to 47.2 eV upon stepwise Mn deposition due to charge transfer, e.g. Schottky barrier (SB) formation. The splitting of the Mn-2p doublet amounts to 11.2 eV and the Mn-$2p_{3/2}$ peak has a BE of 638.7 eV, these values corresponding to metallic manganese. The work function of the Mn films with the thickness of 1 nm is 3.4 eV and slightly decreases to 3.2 eV with further overlayer thickness. The SB height of the interface is determined to be 1.2 eV. The Mn films show no LEED patterns. The XPS results, generally, show the absence of any interfacial compound formation.

Keywords: semiconductor; GaN; Mn thin films, Mn/GaN interface; valence band; photoelectron spectroscopy

---

*Corresponding author: Milosz.Grodzicki@uwr.edu.pl

**Some work on this system was done during a research stay at the Faculty of Science, SEES, University of Portsmouth, Portsmouth, United Kingdom.

Introduction

Gallium nitride (GaN), a semiconductor with a wide band gap of 3.4 eV, attracts great interest of the electronic industry. The crystals have been used for fabricating electronic devices in many fields, such as: high-power, high-frequency as well as optoelectronic [1–3]. This is due to the great physical properties of GaN [4]. In spite of the fact that GaN crystals have been present in science and technology for decades, fundamental research of such systems and the participation of this semiconductor in varied disciplines of science, such as electronics, physics and chemistry continue to be of enormous interest [5–7]. Manganese (Mn) is found to be a very attractive metal to use with GaN crystals in purpose to form a ferromagnetic semiconductor and thus to create hybrid systems with a spintronic potential [8,9]. In regard to this, the Mn/GaN interface is being widely investigated, but most works pertain largely to magnetic properties, while the physicochemical properties of the growing system are omitted. Reports facing surface properties of Mn films on GaN crystals are mainly performed on $(000\bar{1})$ surface and concern ultra-thin coverage [10–14]. Generally, those papers contain the structural analysis performed by STM technique except the work by Kowalik et al. [10] which was carried out by means of synchrotron radiation, where the investigation of the behaviour of Mn adlayers on GaN was observed by the Ga-3d semi-core level line and the valance band.

Herein we report the results of our study of Mn films deposited onto the (0001) surface of non-doped GaN substrate kept at room temperature (RT), under UHV conditions. The early stage of Mn/GaN interface formation was characterized in situ by employing surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and low-energy electron diffraction (LEED).

Materials and methods

Samples, around 10×5 mm^2 in size were cut out from GaN(0001)/Al_2O_3 (TDI Inc.) wafers to be applied as substrates for these studies. The wafer was terminated with an atomically flat epitaxial GaN layer, non-doped, 10-μm thick. The measurements were performed in situ under UHV by means of the surface-analysis system. The UHV chamber is fitted with a twin-anode non-monochromatic radiation source, i.e with Mg K_α (1253.6 eV) and Al K_α (1486.6 eV) lines and also a UPS source with He I (21.2 eV) excitation line from a DC discharged lamp. A hemispherical electron energy analyser (Phoibos 100, Specs) with entrance normal to the substrate surface acquired photoelectrons with a pass energy of 10 or 2 eV and step size of 0.1 or 0.025 eV from core level lines or valence band, respectively. All binding energies of obtained spectra are referenced to the Fermi level (E_F), which was determined from a clean reference Au sample and additionally (to control) from a relatively thick Mn film deposited directly onto the GaN substrate. The UV spectra were also measured with –5 V and –10 V bias to obtain a clear onset of photoemission, which corresponds to the vacuum level (E_{VAC}) of the sample. To analyse recorded spectra the CasaXPS software were used, and the fitting of peaks was done using Gaussian and Lorentzian line shapes and a Shirley-type background. The photoelectron spectroscopies were used for determining chemical and electronic properties of the Mn/GaN interface. Additionally the LEED was used to structural analysis, diffraction patterns were collected in the energy range 0-300 eV with a step of 0.5 eV and were recorded by a CCD camera.

Prior to the experiments the samples were ex situ degreased in alcohol, next rinsed with distilled water and dried in air, then mounted on the Mo plates and placed into the UHV chamber with a base pressure ≤ 1×10^{-10} Torr. Next the initial bare surfaces were obtained by degassing by means of cycles of annealing at temperatures of up to 750ºC, upon which manganese (99.95% purity, MaTecK) films were deposited from a water cool electron beam evaporator. The temperature of samples was measured by an emissivity-corrected pyrometer. All the measurements were done at RT.

Results and discussion

The XPS measurement shows that after thermal treatment the Ga-rich GaN(0001) surface with a low oxygen content and with a vary trace amount of carbon (at the limit of experimental sensitivity) were obtained. Peak intensity for oxygen and carbon contaminants under annealing decreased significantly. The LEED pattern exhibits clear and strong intensity spots corresponding to the (1×1) structure as is shown in Fig. 1, even though the surface is enriched with gallium. This structural behaviour of the gallium-rich GaN(0001) surfaces has already been clarified and published elsewhere [15,16]. The evolutions of XPS spectra of the Ga-3d, the N-1s, Mn-3p for the Mn/GaN(0001) system with the manganese overlayer thickness are shown in Fig. 2. Analysis of photoelectron lines for the bare substrate shows that the Ga-3d semi-core level line with the full width at half-maximum (FWHM) of 1.65 eV is located at 20.3 eV. The peak contains four components, the major one being from the GaN compound, the two others corresponding to Ga-O, Ga-Ga bonds and the last one coming from the N-2s state. The results are consisted with other papers [6,17]. The N-1s core level line with FWHM of 1.15 eV consists of two elements: the main line is connected to N-Ga bonds, and the second to NH_x compound. After the deposition of the Mn film the Ga-3d peak shifts towards a lower binding energy, finally reaching the position of 19.8 eV, with the N-1s peak behaving similarly. The FWHMs of each are slightly elevated by about 0.1 eV. The Mn-3p line also shifts towards a lower binding energy and its final position is 47.2 eV and its FWHM equals 2.5 eV.

The shifts of the peaks are associated with the formation of a Schottky barrier at the phase boundary, which is caused by the transfer of charge until the E_F levelled in both materials. Taking account that the shift value for all the peaks is the same and their FWHMs remain unchanged (within the measurement accuracy which is 0.1 eV) the reaction between Mn and Ga-rich (0001) surfaces at the very early stage of the interface formation can be excluded and is not like that of the (000-1) surface according to Kowalik et al [10]. The measured photoelectrons from the Ga-3d state using standard radiation sources have high kinetic energy, therefore it can be surmised that sensitivity to the surface physicochemical changes is small, but to avoid this assumption the Ga-2p line was also measured (for which the mean free path electron is much smaller). The Ga-$2p_{3/2}$ core level line has a BE of 1118.2 eV and 1117.7 eV before and after the Mn deposition, respectively. The value of the Ga-2p shift is 0.5 eV, the

same as in the case of the Ga-3d line. Furthermore the FWHMs of Ga-$2p_{3/2}$ before and after the Mn deposition equal 1.6 ± 0.1 eV, which rules out the inter-facial reaction of atoms at RT. The spectrum of the Mn-2p doublet for the manganese film on GaN(0001) surface is presented in Fig. 3. The splitting of the 2p doublet amounts to 11.2 eV, which is consistent with other literature data [18]. Closer analysis of the Mn-$2p_{3/2}$ state shows that it has the FWHM of 2.0 eV and can be fitted by two components with a binding energy of 638.7 eV and 639.75 eV.

The spectra of the valence band for the bare GaN(0001) surface and that covered with Mn films are shown in Fig. 4. The shape of the curve for the cleaned GaN(0001) surface exhibits electronic behaviour typical of an n-type semiconductor due to the position of the valence band maximum (VBM), which is located 2.7 eV below the E_F. The position is found from a linear extrapolation of the leading edge of the spectrum to the background. The valence band edge is located 17.6 eV above the Ga-3d core level. The value is in good agreement with those reported in our previous papers and other works [19–24] and indicates that the GaN(0001) surface is well prepared. A closer look at the valence band for the bare surface shows that there are four characteristic features. The first two with lower binding energies labelled as A_0 and A_1 come from interaction of the Ga-4s – N-2p and Ga-4p – N-2p states. The other two labelled as B_0 and B_1 have a nature originating from the Ga-3d – N-2 electron levels [25,26]. The GaN(0001) electron affinity (χ) calculated from the equation $\chi = h\nu - W - E_g$ amounts to 3.5 eV, where: $h\nu$=21.2 eV is the photon energy of He I; W=14.3 eV is the spectrum width, the energy difference between the VBM and the cut-off energy of photoemission E_{cutoff}; and E_g=3.4 eV is the band gap width of the semiconductor. The work function (WF) is accounted to be 4.2 eV and was calculated using the basic formula $WF = h\nu - E_{cutoff}$. The UPS measurements allow us to understand the band structure of the substrate, a common effect, which manifests at the semiconductor surface as band bending (BB). This phenomenon results from a charge transfer between the surface and the bulk. It is the consequence of trapping carriers at surface states, which can come from defects at the surface or have an adsorption nature. The band bending can be determined from the equation $BB = (E_F - VBM)_{bulk} - (E_F - VBM)_{surf}$, which has been done with success in our previous paper [24]. The first part $(E_F - VBM)_{bulk}$ is exactly the position of the E_F relative to the VBM in bulk GaN, which lies in the middle of its gap determined based on the free electron model. The second part $(E_F - VBM)_{surf}$ is the value mentioned above and amounts to 2.7 eV. Taking into account the obtained values the downward BB for the substrate is 1.0 eV (see Fig. 5a). The changes appear in the VB spectrum after deposition of the Mn film. For the relatively low

coverage up to 1 nm the characteristic feature with the maximum at 15.4 eV below the E_F (marked by 'B_1'; curve 1 in Fig. 4) that comes from the overlapping of the Ga-3d and N-2s states is further presented. Further deposition of Mn results in the formation of the metallic film, where the Fermi level is clearly evident. The increase of the E_{vac} level reflects the change of the WF, which drops to 3.2 eV for a 2 nm thick film of Mn and remains unchanged with further growth of Mn layers. On the spectrum there are also clearly visible other differences. The two characteristic features marked by 'C' and 'D' emerge at positions 6.5 eV and 10.8 eV, respectively. They come from electron states of Mn-3d.

The energy level diagrams of the vacuum/GaN(0001) and Mn/GaN(0001) interfaces, developed based on above data, are shown in Fig. 5. The LEED spots intensity of (1×1) structure connected with bulk GaN decrease gradually with the increase of the manganese film thickness. No diffraction patterns were observed for Mn films of various thicknesses. This suggests that the Mn layers are inhomogeneous and that perhaps they have a grainy structure starting from the earliest stages of growth, these grains being randomly oriented.

Conclusions

Combined surface-sensitive techniques of XPS, UPS and LEED are employed to investigate the Mn/GaN(0 0 0 1) interface formation at RT. The prepared substrate has a diffraction pattern exhibiting a highly ordered (1×1) surface structure, with an electron affinity of 3.5 eV. After the adsorption of Mn films no LEED patterns are obtained, however the UPS spectra manifest a purely metallic character. The work function of the manganese film of the thickness of 1 nm is equal to 3.4 eV and for thicker coverage (≥2 nm) decreases to 3.2 eV

A chemical interaction at the Mn/GaN(0001) phase boundary at RT can be excluded based on the XPS results and the shifts of peaks should be assigned to the Schottky barrier formation, with a height amounting to 1.20 eV. Additional studies are planned to investigate the physicochemical properties as well structural changes of the Mn/GaN system after annealing.

Acknowledgments

This work was supported by the University of Wroclaw [grant number 1010/S/IFD/18]. The research was also supported by the European Union under the European Social Fund, under

grant POKL.04.01.01-00-054/10-00, which was provided for a research stay at the Faculty of Science, SEES, University of Portsmouth.

Literature

[1] M.S. Shur, R. Gaska, A. Khan, III-Nitride Power Devices - Good Results and Great Expectations, Mater. Sci. Forum. 353–356 (2001) 807–814. doi:10.4028/www.scientific.net/MSF.353-356.807.
[2] M. Asif Khan, Q. Chen, M.S. Shur, B.T. Dermott, J.A. Higgins, J. Burm, W.J. Schaff, L.F. Eastman, GaN based heterostructure for high power devices, Solid-State Electron. 41 (1997) 1555–1559. doi:10.1016/S0038-1101(97)00104-4.
[3] M.C. Schmidt, K.-C. Kim, R.M. Farrell, D.F. Feezell, D.A. Cohen, M. Saito, K. Fujito, J.S. Speck, S.P. DenBaars, S. Nakamura, Demonstration of Nonpolar m-Plane InGaN/GaN Laser Diodes, Jpn. J. Appl. Phys. 46 (2007) L190–L191. doi:10.1143/JJAP.46.L190.
[4] T. Yao, S.-K. Hong, eds., Oxide and nitride semiconductors: processing, properties, and applications, Springer, Berlin, 2009.
[5] T.J. Flack, B.N. Pushpakaran, S.B. Bayne, GaN Technology for Power Electronic Applications: A Review, J. Electron. Mater. 45 (2016) 2673–2682. doi:10.1007/s11664-016-4435-3.
[6] V.M. Bermudez, The fundamental surface science of wurtzite gallium nitride, Surf. Sci. Rep. 72 (2017) 147–315. doi:10.1016/j.surfrep.2017.05.001.
[7] S.L. Kollmannsberger, C.A. Walenta, A. Winnerl, S. Weiszer, R.N. Pereira, M. Tschurl, M. Stutzmann, U. Heiz, Doping-Dependent Adsorption and Photon-Stimulated Desorption of CO on GaN(0001), J. Phys. Chem. C. 121 (2017) 8473–8479. doi:10.1021/acs.jpcc.7b01570.
[8] S.J. Pearton, C.R. Abernathy, D.P. Norton, A.F. Hebard, Y.D. Park, L.A. Boatner, J.D. Budai, Advances in wide bandgap materials for semiconductor spintronics, Mater. Sci. Eng. R Rep. 40 (2003) 137–168. doi:10.1016/S0927-796X(02)00136-5.
[9] T. Dietl, H. Ohno, Dilute ferromagnetic semiconductors: Physics and spintronic structures, Rev. Mod. Phys. 86 (2014) 187–251. doi:10.1103/RevModPhys.86.187.
[10] I.A. Kowalik, B.J. Kowalski, B.A. Orlowski, E. Lusakowska, R.J. Iwanowski, S. Mickevičius, R.L. Johnson, I. Grzegory, S. Porowski, Photoemission study of Mn/GaN, Surf. Sci. 566–568 (2004) 457–461. doi:10.1016/j.susc.2004.05.085.
[11] J. Dumont, B.J. Kowalski, M. Pietrzyk, T. Seldrum, L. Houssiau, B. Douhard, I. Grzegory, S. Porowski, R. Sporken, Atomically flat GaMnN by diffusion of Mn into GaN(000$\bar{1}$), Superlattices Microstruct. 40 (2006) 607–611. doi:10.1016/j.spmi.2006.07.028.
[12] Y. Qi, G.F. Sun, M. Weinert, L. Li, Electronic structures of Mn-induced phases on GaN(0001), Phys. Rev. B. 80 (2009) 235323. doi:10.1103/PhysRevB.80.235323.
[13] A. Chinchore, K. Wang, M. Shi, Y. Liu, A.R. Smith, Spontaneous formation of quantum height manganese gallium islands and atomic chains on N-polar gallium nitride(000$\bar{1}$), Appl. Phys. Lett. 100 (2012) 061602. doi:10.1063/1.3682487.
[14] K. Wang, N. Takeuchi, A.V. Chinchore, W. Lin, Y. Liu, A.R. Smith, Two-dimensional Mn structure on the GaN growth surface and evidence for room-temperature spin ordering, Phys. Rev. B. 83 (2011) 165407. doi:10.1103/PhysRevB.83.165407.

[15] A.R. Smith, Reconstructions of GaN(0001) and (000$\bar{1}$) surfaces: Ga-rich metallic structures, J. Vac. Sci. Technol. B Microelectron. Nanometer Struct. 16 (1998) 2242. doi:10.1116/1.590156.
[16] A.R. Smith, R.M. Feenstra, D.W. Greve, M.-S. Shin, M. Skowronski, J. Neugebauer, J.E. Northrup, Determination of wurtzite GaN lattice polarity based on surface reconstruction, Appl. Phys. Lett. 72 (1998) 2114–2116. doi:10.1063/1.121293.
[17] J. Falta, T. Schmidt, S. Gangopadhyay, C. Schulz, S. Kuhr, N. Berner, J.I. Flege, A. Pretorius, A. Rosenauer, K. Sebald, H. Lohmeyer, J. Gutowski, S. Figge, T. Yamaguchi, D. Hommel, Cleaning and growth morphology of GaN and InGaN surfaces, Phys. Status Solidi B. 248 (2011) 1800–1809. doi:10.1002/pssb.201046574.
[18] B.V. Crist, Handbooks of Monochromatic XPS Spectra: The Elements and Native Oxides, wiley, USA, 2000. https://www.wiley.com.
[19] M. Grodzicki, P. Mazur, J. Pers, J. Brona, S. Zuber, A. Ciszewski, Formation of GaPd2 and GaPd intermetallic compounds on GaN(0001), Appl. Phys. A. 120 (2015) 1443–1451. doi:10.1007/s00339-015-9331-9.
[20] M. Grodzicki, P. Mazur, S. Zuber, J. Brona, A. Ciszewski, Oxidation of GaN(0001) by low-energy ion bombardment, Appl. Surf. Sci. 304 (2014) 20–23. doi:10.1016/j.apsusc.2013.11.146.
[21] M. Grodzicki, P. Mazur, S. Zuber, J. Pers, J. Brona, A. Ciszewski, Effect of annealing on Ni/GaN(0001) contact morphology, Appl. Surf. Sci. 304 (2014) 24–28. doi:10.1016/j.apsusc.2014.01.023.
[22] J.R. Waldrop, R.W. Grant, Measurement of AlN/GaN (0001) heterojunction band offsets by x-ray photoemission spectroscopy, Appl. Phys. Lett. 68 (1996) 2879 –2881. doi:10.1063/1.116355.
[23] V.M. Bermudez, Study of oxygen chemisorption on the GaN(0001)-(1 ×1) surface, J. Appl. Phys. 80 (1996) 1190–1200. doi:10.1063/1.362924.
[24] M. Grodzicki, P. Mazur, A. Ciszewski, Changes of electronic properties of p-GaN(0001) surface after low-energy N+-ion bombardment, Appl. Surf. Sci. (n.d.). doi:10.1016/j.apsusc.2018.01.097.
[25] M.-Z. Huang, W.Y. Ching, A minimal basis semi-ab initio approach to the band structures of semiconductors, J. Phys. Chem. Solids. 46 (1985) 977–995. doi:10.1016/0022-3697(85)90101-5.
[26] W.R.L. Lambrecht, B. Segall, S. Strite, G. Martin, A. Agarwal, H. Morkoç, A. Rockett, X-ray photoelectron spectroscopy and theory of the valence band and semicore Ga 3d states in GaN, Phys. Rev. B. 50 (1994) 14155–14160. doi:10.1103/PhysRevB.50.14155.

Figure captions

Fig. 1. The LEED patterns of bare GaN(0001) surface with (1×1) structure. The images were taken at energy of (a) 45 eV, and (b) 120 eV.

Fig. 2. The XPS spectra of (a) Ga-3d, (b) N-1s and (c) Mn-3p for the Mn/GaN(0001) interface and their evolution with the thickness of deposited Mn films.

Fig. 3. The XPS spectrum of the Mn-2p core level line with its fitting. The mean thickness of Mn film is 5 nm.

Fig. 4. The broad UPS valence band spectrum of the bare GaN(0001) surface and its evolution with Mn over-layer thickness. The spectra were collected with -5 V bias.

Fig. 5. The schematic energy diagram of (a) the vacuum/GaN(0001), and (b) Mn/GaN(0001) interfaces. The Schottky barrier height at the interface is 1.2 eV, more details about its calculation are in the text.

Figures

Fig.1

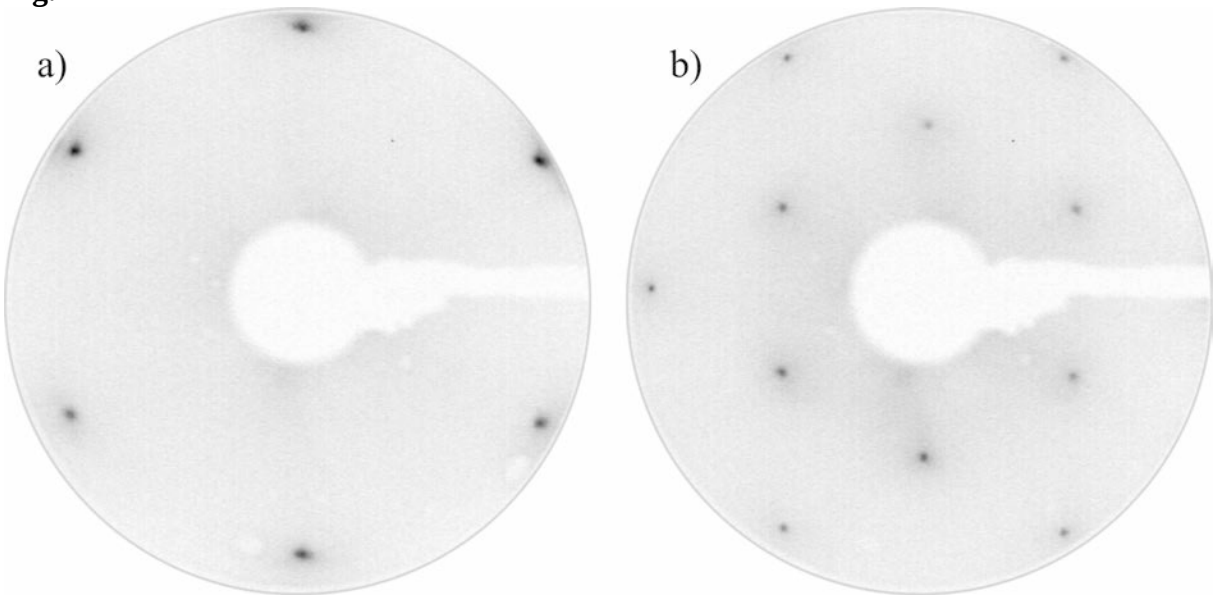
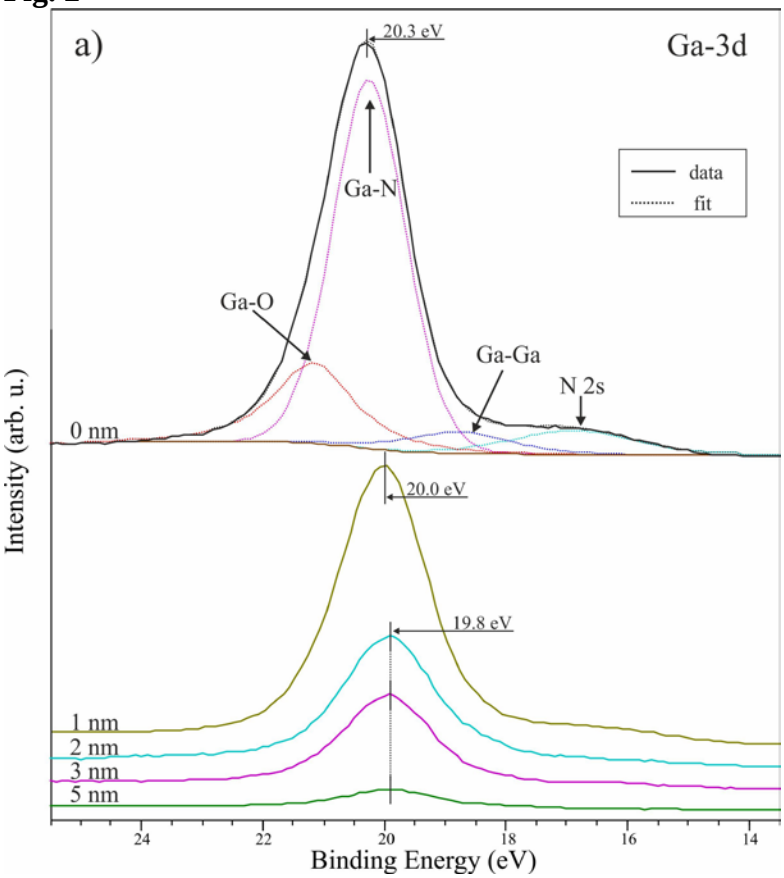


Fig. 2



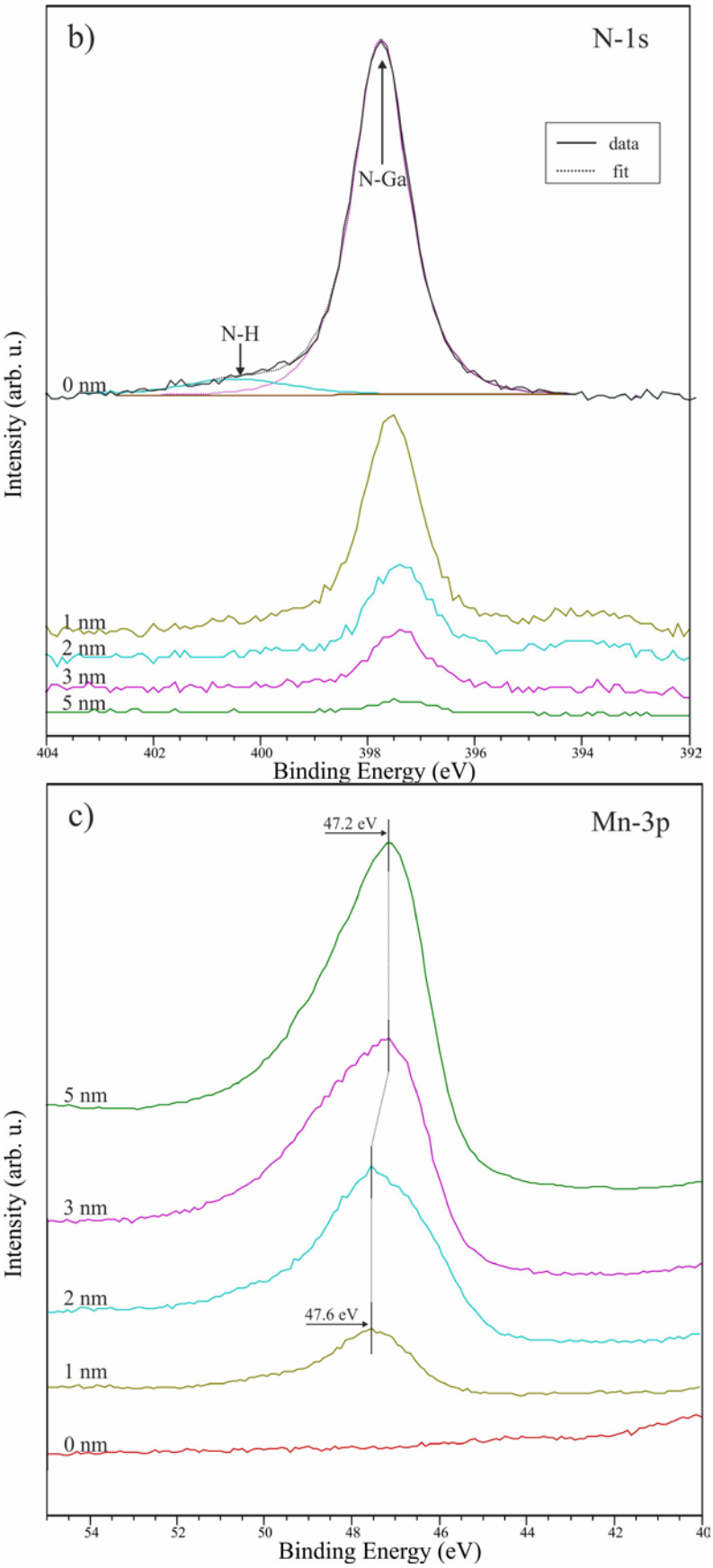

b)
N-1s
data
fit
N-Ga
N-H
0 nm
1 nm
2 nm
3 nm
5 nm
Intensity (arb. u.)
404
402
400
398
396
394
392
Binding Energy (eV)
c)
Mn-3p
47.2 eV
47.6 eV
5 nm
3 nm
2 nm
1 nm
0 nm
Intensity (arb. u.)
54
52
50
48
46
44
42
40
Binding Energy (eV)

Fig.3

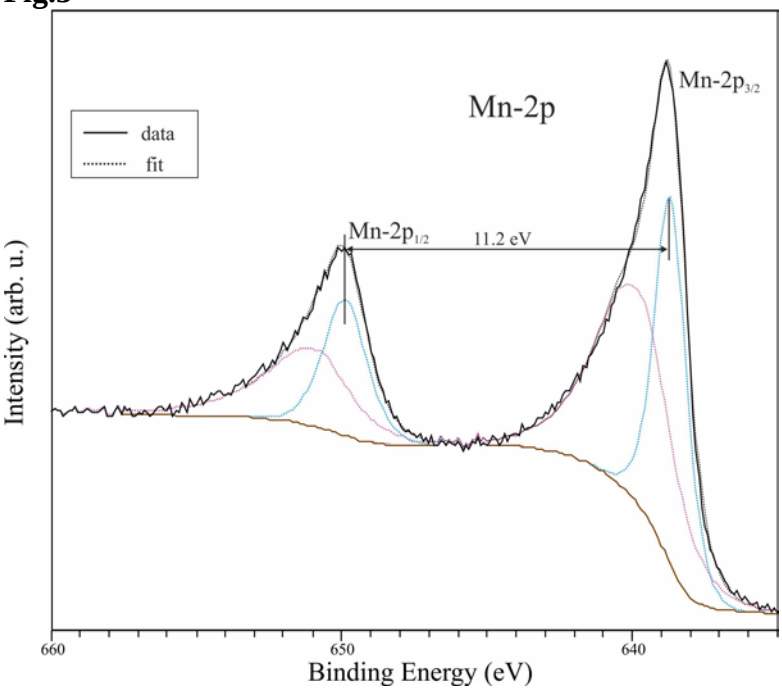

Mn-2p
data
fit
Mn-2p3/2
Mn-2p1/2
11.2 eV
Intensity (arb. u.)
660
650
640
Binding Energy (eV)

Fig.4

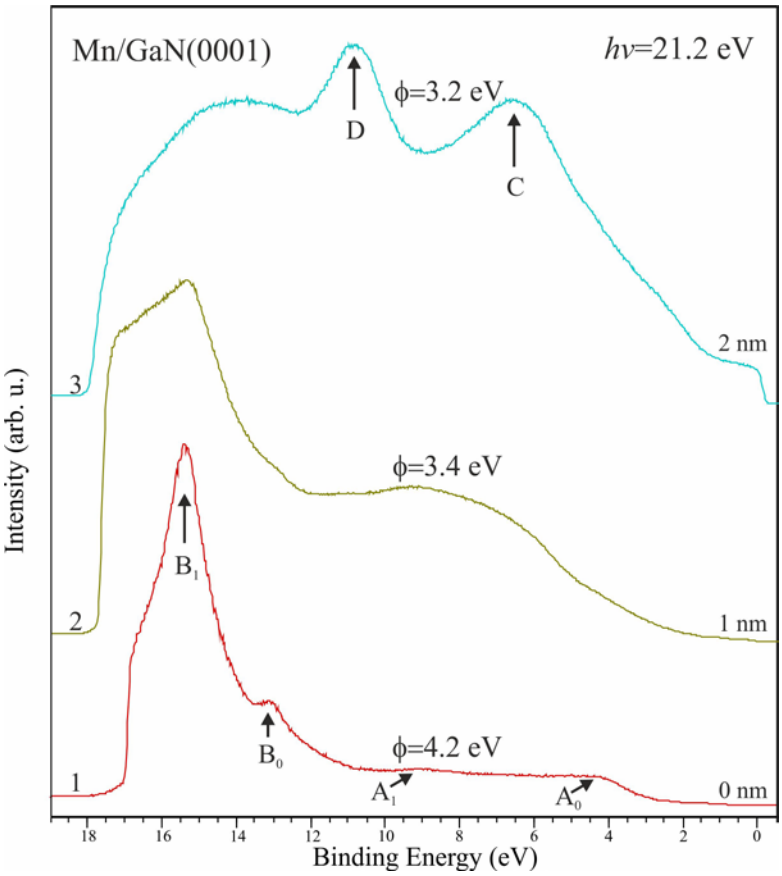
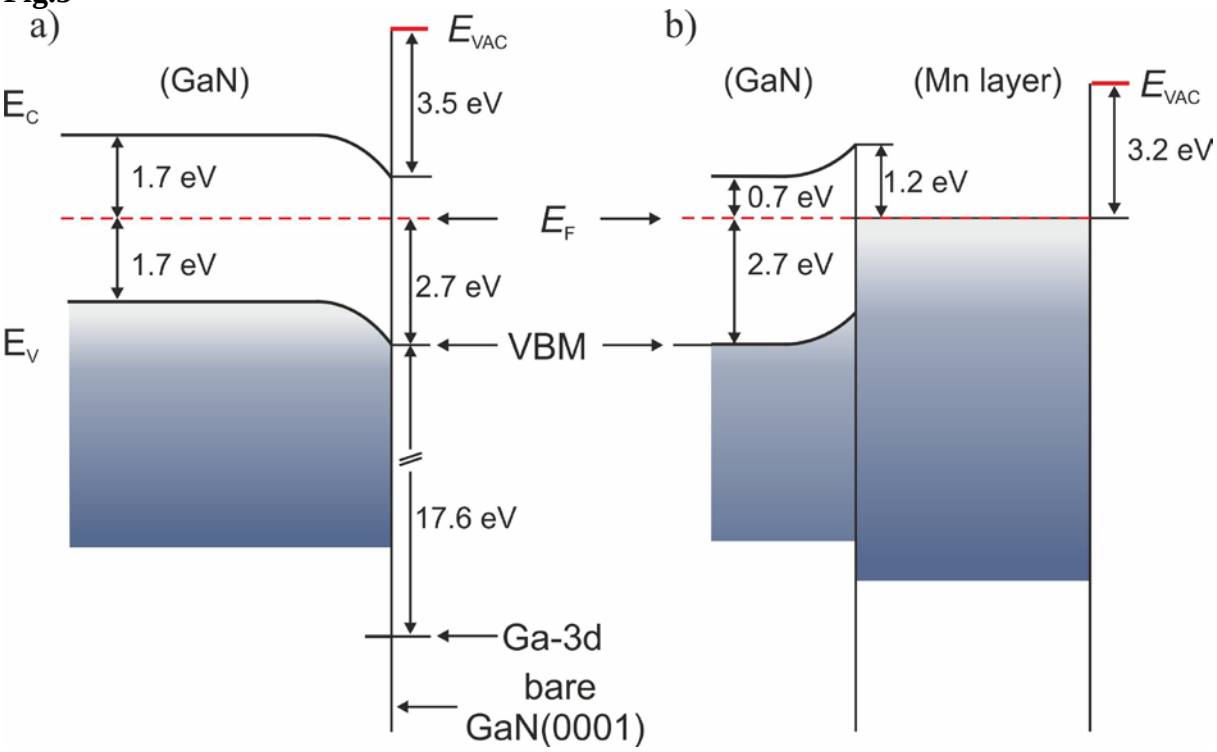

Mn/GaN(0001)
hv=21.2 eV
ϕ=3.2 eV
D
C
2 nm
3
ϕ=3.4 eV
B1
2
1 nm
B0
ϕ=4.2 eV
1
A1
A0
0 nm
Intensity (arb. u.)
18
16
14
12
10
8
6
4
2
0
Binding Energy (eV)

Fig.5


a)
(GaN)
E_{VAC}
3.5 eV
E_C
1.7 eV
1.7 eV
E_F
2.7 eV
E_V
VBM
17.6 eV
Ga-3d
bare
GaN(0001)
b)
(GaN)
(Mn layer)
E_{VAC}
3.2 eV
0.7 eV
1.2 eV
2.7 eV