Fermi Level Movements at the Transition Metal/GaN Interface

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One of the wide band gap III-V compound semiconductor, GaN, is expected to be utilized for the high-functional optical device due to its superior chemical-stability. In the present study, it has been investigated what is the most important factor determining the position of the Fermi level at the interface between GaN and depositing metal through studying interfacial electrical properties, bonding state and thermal stability. Under ultrahigh vacuum, Ni, Pd, Pt, Au, Ti, Cr and Al were *in-situ* deposited on both types of GaN grown by MOCVD and studied by photoemission, AES depth profiles and AFM. Through the band bending analysis, it can be recognized that *unless the new layers, like either TiN or CrGaN, are not formed, the band bending depends more upon the solid state electronegativity than the work function of the contacting metal.* Most of metals were uniformly deposited, and especially Ti, Cr, and Al were reacting with GaN at the depositing instant resulting in the novel phase mixing with N and Ga segregation. On the other hand Ni, Pd, and Pt did not form any nitride and their on-set temperature for reacting with GaN were different ($T_{Ni}<T_{Pd}<T_{Pt}$).

. The pre-requisite condition for GaN application to the laser diode operating at room temperature is to achieve the low-resistive ohmic contact. It has been reported that the ohmic contacts with n-type GaN are achieved through contacting Ti and Al [1-3]. Since the N vacancy near the GaN interface can act as an n-type carrier, it is relatively easy to make a low resistive and thin layer using contacting metal like Ti which forms a nitride with N from the underlying GaN. The remaining Ti and covering Al can form an alloy like Al_3Ti, which has resistance to oxidation. On the other hand, such an advantage of n-GaN can act as a limiting factor to p-GaN ohmic contact. Therefore the metal which does not form nitride can be a candidate for a contacting metal forming an ohmic contact on the p-type GaN. Besides such an interfacial nitride formation problem, the work function (Φ) or the solid state electronegativity (EN) of the contacting metal should be also considered, since it has been reported that the Fermi level of GaN is not pinned in the gap at the metal/GaN contact [2,4]. In the late sixties Kurtin et al. proposed that the Schottky barrier of the strong ionic semiconductor like GaN should have the barrier height proportional to the difference between the metal work-function and the GaN electron affinity [5]. More recently, Kampen and Mönch suggested that the Schottky barrier height (SBH) is determined by the metal induced gap states as well as the solid state electronegativity difference of the contacting metal and GaN [6]. Henceforth, for ohmic contact on p-type, the

metal with larger work function (or electronegativity) seems to be better since the sum of electron affinity of GaN (4.1 eV) and its band gap (3.4 eV) is larger than the work-function (or electronegativity) of any metal. Therefore, Ni, one of the late transition metal with relatively large work-function (5.1 eV), has been intensively investigated expecting the ohmic contact with p-GaN, since Ni tends to disrupt GaN through postannealing and has been believed not to form any stable nitride. Sheu et al. recently reported that a Ni/Au contact on p-GaN becomes ohmic after annealing at 700 C for 10 min [7]. But the slope of its I-V curve is small (i.e., showing high resistance 1×10^5 Ω). They ascribed such high resistivity to the presence of a resistive Ni_3N phase at the annealed interface, which was deduced by x-ray diffraction (XRD) results. More recently, Kim et al. reported that the drastic contact resistivity decrement to 4.3×10^{-4} Ωcm^2 from Pd/Au deposited on p-GaN after surface treatment using boiling aqua regia (HNO_3:HCl=1:3) for 10 min[8]. They interpreted that such drastic resistivity decrement is due to surface oxide removal. But they did not report on the thermal stability of this structure, which might be critical to utilize the non-disruptive films composed of late-transition-metals. Up to now, in the ohmic contact studies on p-GaN, it is not clear which is the determining factor to achieve the stable and low-resistive ohmic contact among the possible obstacles: *high doping concentration* of bulk p-GaN, *low N vacancy concentration* at the reacted interface, *low donor-like impurity concentration* at the interface, and *high work-function (or electronegativity) of contacting metal.*

The crystalline GaN surfaces were grown on sapphire substrates at LG Corporate Institute of Technology by metalorganic chemical vapor deposition (MOCVD). The p-type(n-type) surface was Mg(Si) doped with carrier concentration of 1.0×10^{17} cm^{-3} (9.0×10^{17} cm^{-3}). Prior to introducing them to the ultrahigh vacuum (UHV) chamber, they were degreased and etched with buffered HF (H_2O:HF=1:1) for 10 min[9]. Finally they were rinsed with deionized water, blow-dried with high purity Ar, and quickly transferred to the UHV chamber. The GaN surfaces were mounted on a Ta sheet and clipped with the same Ta from the front side to prevent charging during surface analyses. Preannealing and postannealing, that is, annealing prior to and after metal deposition respectively, were conducted by resistive heating of this Ta plate contacting with sapphire substrates. Metal wires wrapped on W baskets were thermally evaporated and a quartz thickness monitor was employed to estimate evaporation. The base pressure of analysis chamber was kept below 5.0×10^{-11} Torr while it temporarily increased up to 3.0×10^{-9} Torr during evaporation.

Using x-ray photoelectron spectroscopy (XPS) equipped with a monochromatic Al $K\alpha$ source and a multi-channel detector, the core levels such as Ga 3d, Ga 2p, N 1s, and valence band were obtained prior to vacuum preannealing. In addition to photoelectron spectra, the Auger electron spectroscopy (AES) survey was also obtained. In order to remove possible contaminating species adsorbed in air, the sample was preannealed under UHV at 650 C for 1 min. The same spectra set were obtained to observe such preannealing effect. Then the metal was

thermally evaporated and the surface morphology was *in-situ* checked with scanning electron microscopy. The same spectra set including metal core levels were obtained, and the AES depth profile of metal-deposited surface was also obtained. Since the scanning electron microscope combined with Ar sputtering gun and the monochromatic x-ray source about 1 mm wide were used, this sputtered area can be easily avoided in the subsequent analysis.

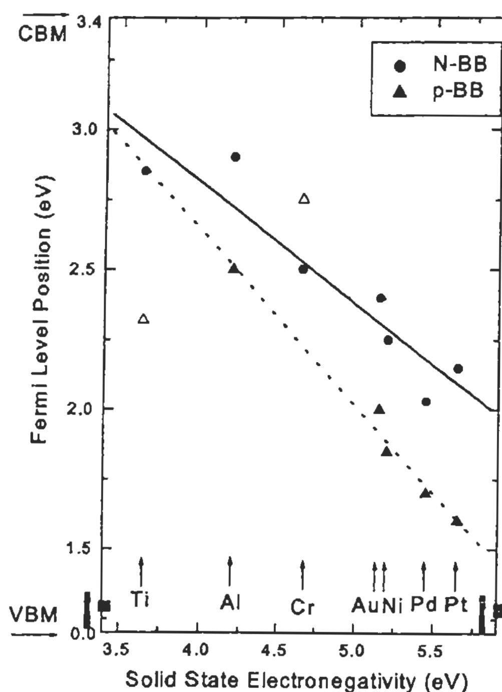

Fig. 1. Fermi level positions versus Solid State Electronegativity of deposited metals.

In order to understand the origin of the band bending in the metal contacted GaN system, the band bending results of metals such as Al, Ti, Cr, Au, Ni, Pd and Pt are shown in Fig. 1 and their analysis results are listed in tables 1 and 2. Since all the experiments have been conducted under the same condition, it is reasonable to compare the results. It can be easily recognized that the Fermi level is not pinned at a certain position in the band gap as we have already stated. As previously introduced, there are two parameters related to the metal, one is the solid state electronegativity difference between two contacting materials and the other is the metal work function. Since these two parameters have a similar trend to vary, that is, most of metals with lower(higher) solid state electronegativity have relatively lower(higher) work function [10,11], the band bending change relative to both parameters appears to be same for most of metals except a few cases although their origins are apparently different. Therefore it is useful to compare the band bending dependency on both parameters using the same results listed in table 1.

Table 1. List of band bending value. **Φ:** Metal work function [10], **Δ:** Solid state electronegativity [11], **n-BB:** Band bending of metal deposited n-type GaN, **n-ΔBB:** Band bending change after metal deposition relative to that of preannealed n-type GaN, **p-BB:** Band bending of metal deposited p-type GaN, **p-ΔBB:** Band bending change after metal deposition relatve to that of preannealed p-type GaN. (unit: eV)

Metal	Φ	Δ	n-BB	n-ΔBB	p-ΔB	p-ΔBB
Al	4.28	4.20	0.50	0.00	2.50	0.85
Ti	4.33	3.64	0.55	0.17	2.32	0.34
Cr	4.50	4.65	0.90	0.23	2.75	0.58
Au	5.10	5.15	1.00	0.58	2.00	0.25
Pd	5.12	5.45	1.37	0.72	1.70	0.19
Ni	5.15	5.20	1.15	0.65	1.85	0.05
Pt	5.65	5.65	1.25	0.95	1.60	-0.34

For n-type GaN surfaces, for example, the

absolute band bending (n-BB) ranges from 0.5eV of Al to 1.37 eV of Pd. The reason why the columns of *net band bending* change are added in the table 1, is that the initial band bending of each surface prior to metal deposition is not exactly same. Therefore, if we compare the band bending of metal deposited surface with that of the preannealed surface, the net metal contact effect will be singled out, assuming the Fermi level of pinned portion is not affected by the deposited metal. Then, as listed in the table 1, such *net band bending change* ranges from 0 eV(for Al) to 0.95 eV(for Pt) for n-type. For p-type GaN surfaces, the *absolute band bending* ranges from 1.55 eV(for Pt) to 2.75 eV(for Cr) and the *net band bending change* ranges from -0.34 eV(for Pt) to 0.85eV(for Al). In table 2, the best line fitting results are listed, that is, the slope and the deviation from the line using the data listed in table 1 are listed. The deviation was obtained by averaging the square of the difference between the measured band bending and the band bending value on the fitted line, and then square-rooting this average value.

First, in table 2, any slope of data plotted relative to the metal work function (Φ) is far below 1, which implies that the ideal Schottky model or the Kurtin's model cannot be applied to these systems. Second, as listed in the first parenthesis of table 2, the line fitting by the model using the metal induced gap states (MIGS)[12] combined with the solid state electronegativity difference[6], that is, the line passing through the charge neutrality level (CNL) point (5.35,1.1) of n-GaN and having the slope of 0.29, is not a best fitting (i. e., 0.123). In this line fitting, Ti, Cr and Au were almost on the line but Ni, Pd and Pt were above the line and Al was below the line.

Table 2. List of the band bending deviation and slope. Band bending deviation (defined by $[\Sigma\{\text{band bending data-band bending on the best fitted line}\}^2/\text{number of metals}]^{0.5}$ eV) from the best fitted line and its slope when the band bending (n-BB, n-ΔBB, p-BB, p-ΔBB) is plotted with respect to the solid state electronegativity (Δ) [11]or the work function (Φ) of the deposited metal [10].

X	Y	Deviation (eV)	Slope(Y/X)	Remark
Δ	n-BB	**0.100** (0.123)	0.39(0.29)	(MIGS+Electronegativity)
Δ	n- ΔBB	0.220 (**0.034**)	0.65	(Ti is excluded)
Δ	p-BB	0.296 (**0.045**)	-0.66	Ti is excluded (Both Ti and Cr are excluded)
Δ	p- ΔBB	0.125	-0.77	Ti is excluded
Φ	n-BB	0.147	0.57	
Φ	n- ΔBB	0.055 (0.046)	0.66	(when only Ti is excluded)
Φ	p-BB	0.170 (0.118)	-0.76(-0.76)	Ti is excluded (Both Ti and Cr are excluded)
Φ	p- ΔBB	**0.059**	-0.81	Ti is excluded

If this model is applied to p-type, that is, if the line should pass through the charge neutrality level point (5.35,2.32) of p-GaN and have the slope of -0.29 [6], all the points were far under the line except Cr, and the deviation was about 0.400 eV. Hence it was not even listed in the table 2. If data are fitted relative to the

electronegativity without fixing CNL and the slope, the best fitted line pass through (5.35, 1.2) and its slope is 0.39 for n-type GaN. For p-type, the best fitted line has a steep slope, −0.66, with its new CNL at 1.74 eV and Al, Au, Ni, Pd and Pt were almost on the line but Ti was at the original CNL (i.e., 2.32 eV) and Cr was 0.55 eV above the line (i.e., more band bending). Therefore, if Ti is eliminated in the n-type fitting, the slope becomes 0.53 and the deviation becomes 0.083 eV (not listed in the table 2). Such a trend becomes more distinct for the net band bending change fitting, as shown in the second row of table 2. These imply that if the slope is so steep that the metal with low electronegativity should have a net negative band bending change, then the net band bending change saturates near zero value for n-type case. Hence even though the unpinned portion is affected by the metal which should induce the negative band bending, the band flattening stops at zero, which indicates that there is a high density state near the conduction band minimum such as N-vacancy state[1]. For p-type case, if Ti (which is 0.6 eV less bending than the fitted line) is not included in the fitting, the deviation is reduced. And additionally if Cr (which is 0.55 eV more bending than the fitted line) is not included, the fitting will becomes much better as shown in the third row. The deviation reduction through eliminating Ti, might be due to the fact that the interface becomes more like TiN/GaN than Ti/GaN resulting in the change of electronegativity difference. And the deviation reduction through eliminating Cr, might be due to n-doping effect of Cr in GaN through partially smearing into GaN substrate and forming CrGaN ternary phase at the interface[13]. Through this band bending analysis it can be recognized that *unless the new layers, like either TiN or CrGaN, are not formed, the band bending depends more upon the solid state electronegativity than the work function of the contacting metal.* If we calibrate the initial band bending state prior to metal deposition, such dependency can be seen more clearly. Such requirement for calibration to observe the band bending dependency must be due to the limit of the MOCVD grown GaN surface to be cleaned in the air and without a perfect buffer layer. Besides such imperfection of the surface, however, there are a few more questions in applying this model to the present data, such as which is the correct charge neutrality level of p-type surface and why the line slope (about 0.66) is much steeper than 0.29.

Based upon the present studies, it has been deduced that, in order to achieve the low-resistive ohmic contact for p-type GaN, methods to apply the metal with relatively high electronegativity without losing N species through keeping the film-like morphology and to suppress undesirable n-type doping like O species, should be devised. It seems that the Fermi level of GaN is not pinned at a certain energy level in the gap. Also, since the Schottky barrier height difference is not exactly matching with the work function difference of contacting metals, i. e., the Fermi level of metal/GaN follows neither the ideal Schottky contact model nor the Kurtin's model even though GaN belongs to a strong ionic semiconductor. The barrier height depends more upon the solid state electronegativity than the work-function of the contacting metal. Hence, the Pt layer induced the largest band

bending change for n-type GaN and the largest band-flattening change for p-type than any of the other metal layer.

In order to achieve low-resistive ohmic contact on GaN, especially on p-type GaN using late-transition-metals, a few critical problems should be clarified. Firstly, late transition metals such as Ni, Pd and Pt cannot be postannealed at relatively high temperature to improve the contact property due to their weak thermal stability on GaN. Therefore an additional metal with small surface free energy and forming an alloy with the deposited late-transition-metals should be added to relieve the strain from the substrate, that is, to overcome the thermal expansion coefficient difference between the metal film and GaN. Since the thermally stable overlayer efficiently blocks N diffusion from the substrate to the vacuum, the undesirable n-type doping generated by N-vacancies could then be avoided. Secondly, the remnant species such as O, C, and F after chemical etching should be removed prior to metal deposition in order to precisely control the barrier height depending upon the solid state electronegativity. Thirdly, there is a limit to reduce the Schottky barrier height of p-GaN through contacting high elctronegativity metals, which suggests to devise methods for interfacial high doping to induce carrier tunneling.

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