X-ray absorption spectroscopy investigations on oxidized Ni/Au contacts to *p*-GaN

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X-ray absorption spectroscopy was used to investigate the electronic structure of as-deposited and oxidized Ni/Au contacts to *p*-GaN and to elucidate the mechanism responsible for low impedance. X-ray absorption near edge spectra of Ni *K*- and $L_{3,2}$-edges clearly indicate formation of NiO on the sample surface after annealing. The reason for low impedance may be attributed to increase in hole concentration and existence of *p*-NiO layer on the surface.

Keywords: *p*-GaN, X-ray absorption, Ni/Au contacts, *p*-NiO

1. Introduction

Metal-semiconductor contact is an essential factor that determines the characteristics of both optoelectronic and microelectronic devices. Selection of metal contacts needs proper understanding of their electronic structure (Maeda *et al.*, 1999). Several combinations of metal contacts have been attempted for both *n*- and *p*-type GaN (Pearton *et al.*, 1999; Jain *et al.*, 2000). The most widely used ohmic contacts to *n*-type GaN are based on an Al/Ti bilayer (Lin *et al.*, 1994). Identifying suitable ohmic contact for *p*-GaN has been a major problem. Recently, Ho *et al.*, succeeded in making a very low specific contact resistance lower than 1 x 10^{-4} Ω cm^2 to *p*-GaN by oxidizing Ni/Au bilayer metallization (Ho *et al.*, 1999). This has motivated many investigations on Ni/Au contacts to *p*-GaN (Chen *et al.*, 2000). Ho *et al.*, proposed that during oxidization of Ni/Au contacts to *p*-GaN, Ni diffuses out and oxidizes to form crystalline NiO layer. They attributed the low resistance ohmic contact to the formation of *p*-NiO preferably with Ni in 3+ state or presence of interstitial oxygen (Ho *et al.*, 1998). The reason for these excellent electrical properties promoted this detailed x-ray absorption spectroscopic investigation to understand their electronic structure. In this process, one can also look for signature of Ni^{3+} state and how the x-ray absorption spectrum of *p*-NiO is different from insulating NiO thin films. Such study not only can elucidate the mechanism for the low impedance but also provide a way to technology to benefit from this research.

In this paper, we report x-ray absorption spectroscopic investigations using Ni *K*- and $L_{3,2}$-edges on as-deposited and oxidized Ni/Au contacts to *p*-GaNs and understand the electronic structure of these contacts.

2. Experimental

The GaN samples used in this study were grown by a low pressure metalorganic chemical vapor deposition method on sapphire (0001) substrates. Details about preparation and characterization of these samples are given elsewhere (Ho *et al.*, 1999). For the present investigation, we have selected one as-deposited sample of *p*-GaN/Ni(100Å)/Au(50Å) and two oxidized samples: (a) *p*-GaN/Ni(50Å)/Au(50Å) and (b) *p*-GaN/Ni(100Å)/Au(50Å). Annealing was done in air at 500°C. Note that Au thickness is constant in all these samples. It was reported by Ho *et al.* that annealed samples with 50Å of Ni thickness give very low contact resistance compared to samples with Ni of 100Å (Ho *et al.*, 1999). To examine the effect of thickness on annealing process and the variation in electronic structure, we selected samples of different Ni thickness.

Room temperature x-ray absorption spectra were recorded using the facility at the Synchrotron Radiation Research Center, Hsinchu, Taiwan, operating with electron energy of 1.5 GeV and a maximum stored current of 200mA. For all samples, while Ni *K*-edge spectra were obtained from Wiggler beamline in fluorescence mode, the Ni $L_{3,2}$-edges from high-energy spherical monochromator beamline in sample drain current mode in vaccum better than 10^{-9} torr. Spectra for reference samples namely Ni foil and NiO thin film were also recorded.

3. Results and Discussion

Fig.1 shows the normalized x-ray absorption near spectra of Ni *K*-edge obtained for as-deposited and oxidized samples of Ni/Au contacts to *p*-GaNs. Ni foil and NiO thin film were used for reference. Different threshold energy inflection points in the spectra provide the differences in the electronic configurations present in the ground state and on the formal Ni oxidation states. As evident from the figure, the spectral features of as-deposited sample resemble Ni foil. It shows that Ni layer deposited on *p*-GaN remains as metal layer and there is no trace of NiO. Ho *et al.*, proposed that interdiffusion of Ni and Au atoms occurs during annealing process and the grain boundaries serve as quick diffusion channels for out-diffusion of Ni atoms to the surface at this temperature (Ho *et al.*, 1999). It was also emphasized that *p*-NiO is formed possibly due to increasing Ni^{3+} ions by introducing Ni^{2+} vacancies and or interstitial oxygen. The low specific contact resistance of the oxidized Ni/Au metallization scheme was attributed to the high conductivity of Au islands and the low contact barrier of *p*–NiO to *p*-GaN.

From the figure, the spectral features of oxidized samples are very much similar to NiO spectra indicating formation of NiO after annealing at 500°C in air. Another point needs to be noted that annealed samples do not show any pre-edge peak as observed in NiO thin film (shown by arrow mark). The energy of the main peak does not show any shift for these annealed samples indicating that Ni is in divalent state. This is shown in the figure by drawing a dashed line. From spectroscopic data, one would expect considerable amount of shift in peak position if Ni^{3+} were present in these compounds (Garcia *et al.*, 1995). We find no evidence for presence of Ni^{3+} in these oxidized samples.

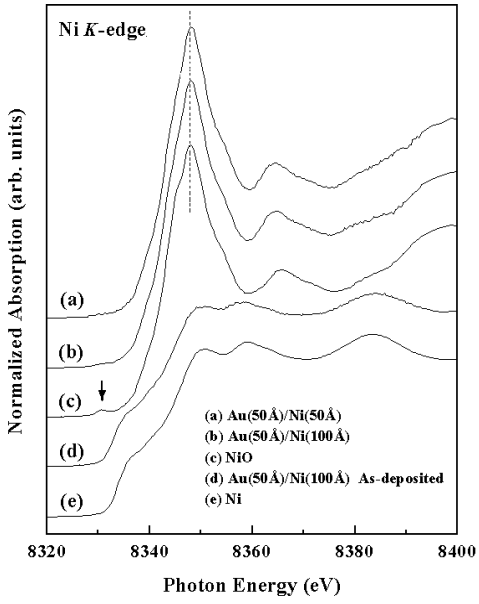

Figure 1
Normalized x-ray absorption spectra (obtained in fluorescence mode) of Ni *K*-edge of as-deposited and oxidized samples of Ni/Au contact to *p*-GaN along with Ni and NiO thin films.

The extended x-ray absorption fine structure (EXAFS) region is useful to extract the information about interatomic distances between Ni and O. Fig. 2 shows the Fourier transform (FT) amplitudes of the EXAFS $k^2\chi$ data at the Ni *K*-edge for oxidized samples of *p*-GaN samples with NiO. The inset represents the Ni *K*-edge EXAFS oscillations $k^2\chi$ data which indicates that noise in the data is low. The position of the FT peaks do not represent the real atomic distances as the FT plotted in Fig. 2 is not corrected for the photoelectron backscattering phase shifts with the motivation of presenting the raw data. As shown in the figure, even with qualitative analysis, one notices the change in the bond length between Ni and O. The *p*-*d* hybridization depends on the energy separations between transition metal 3*d* and O 2*p* states and the bond lengths. It is known that the square of the hybridization coupling constant, V_{pd}^2 is proportional to (r_d^3/d_{NN}^7), where r_d and d_{NN} are the transition metal *d*-orbital radius and the 3*d* transition metal-nearest neighbor bond length respectively (Harrison, 1980). Based on this relation, decrease in bond length between Ni and O enhances the *p*-*d* hybridization. Such hybridization arises only when the states are directed towards each other leading to greater charge transfer. In other words, an increased overlap of the electron's wave functions occurs due to the decreased interatomic distance. Annealing the samples lead to increase in hole concentrations and form NiO of *p*-type. Due to increase in hole concentrations, the specific contact resistance is reduced considerably.

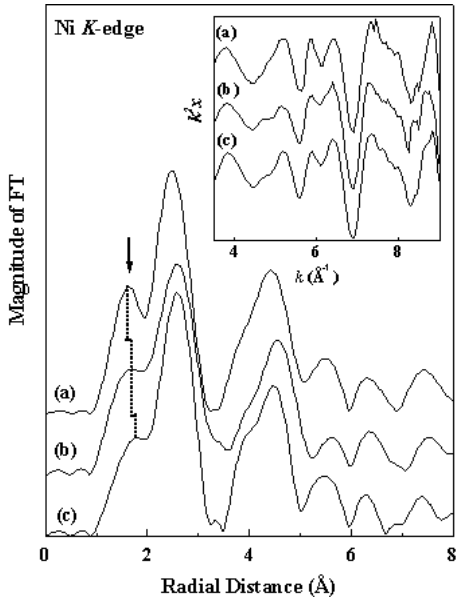

Figure 2
Magnitude of the Fourier transform amplitudes of the EXAFS $k^2\chi$ data at the Ni *K*-edge for (a) *p*-GaN/Ni(50Å)/Au(50Å), (b) *p*-GaN/Ni(100Å)/Au(50Å), and (c) NiO thin film. The Fourier transform has been performed from 3.5 to 9Å^{-1}. The inset represents the Ni *K*-edge EXAFS oscillations $k^2\chi$ data.

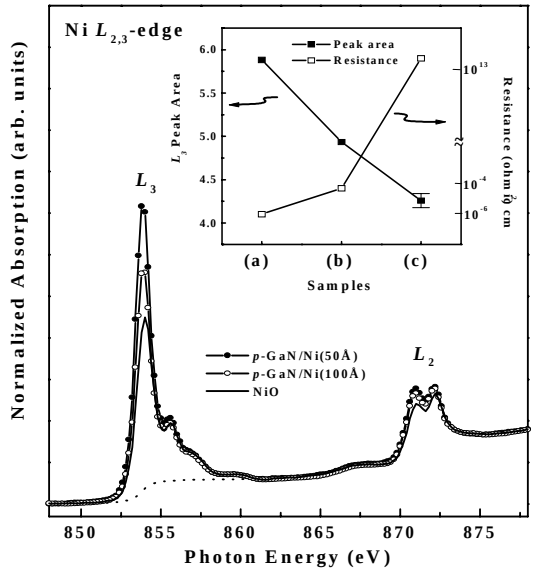

Figure 3
Normalized x-ray absorption spectra of Ni L_3-edge for samples (a) *p*-GaN/Ni(50Å)/Au(50Å), (b) *p*-GaN/Ni(100Å) /Au(50Å), and (c) NiO thin film. Inset shows the correlation between contact resistance of above samples and Ni L_3 peak area. Note that the axis is broken to show the high resistance of NiO thin films.

In particular, the Ni $L_{3,2}$-edge gives information on the Ni electronic structure including the presence and the amount of hole states. The area under this region directly indicates hole concentration (Srivastava *et al*., 1997). We measured the Ni $L_{3,2}$-edge to get additional information about the amount of holes and check whether there is any relation with the thickness of Ni and specific contact resistance. Fig. 3 provides the normalized x-ray absorption spectra of Ni L_3-edge. The area under this region was extracted by using the continuous step of the arctangent function centered at the maximum height of peak. We notice that the integrated area from 850 to 863 eV of L_3 edge reason is significantly higher in the oxidized samples as compared to NiO. Inset in the figure shows the relation between the area under L_3 edge region and specific contact resistance of the samples investigated. The annealed samples show very low resistance and more area than NiO thin film. NiO is an insulator and we considered its resistance in the order of $\sim 10^{10}\ \Omega\ cm^2$. From the measurements carried out by Ho *et al*., it is known that the specific contact resistance is also dependent on Ni thickness. The oxidized sample having Ni(50Å) has a maximum peak area and possesses maximum hole concentration consistent with the very low specific contact resistance. The above studies clearly demonstrate the formation of *p*-NiO layer on the sample surface after annealing and increase in hole concentration is responsible for low specific contact resistance. Annealing temperature and Ni thickness determine the oxygen stoichiometry of these samples and hence the specific contact resistance.

4. Conclusion

The electronic structures of as-deposited and oxidized Ni/Au contacts to *p*-GaNs were investigated using x-ray absorption spectroscopy. NiO is formed after annealing the samples at 500^o C in air and there is no signature of Ni^{3+} state. Decrease in bond length between Ni and O increases *p-d* hybridization and leads to more holes. Such a system is *p*-NiO. The low contact resistance is attributed to the decrease in bond length between Ni and O and the existence of *p*-NiO layer. Annealing temperature and Ni thickness determine the oxygen stoichiometry of these samples. Our findings will inspire studies on the role of *p*-NiO in determining physical properties of semiconductors and in other materials.

Acknowledgment

One of us (K.A) is thankful to Prof. G. K. Mehta, Director, Nuclear Science Center, New Delhi for granting leave and encouragement. The authors (K. A. and W. F. P.) wish to acknowledge support by the National Science Council of the Republic of China under Contract No. NSC-89-2112-M-032-008. The excellent cooperation during the beam time from SRRC staff is highly appreciated.

References

Chen, L. C., Ho, J. H., Jong, C. S., Chiu, C. C., Shih, K. K., Chen, F. R., Kai, J. J & Chang, L., (2000). *Appl. Phys. Lett.* **76**, 3703 and references therein.

Garcia, J., Blasco, J., Proietti, M. G., & Benfatto, M. (1995). *Phys. Rev*. B**52**, 15823.

Harrison, W. A., (1980). *Electronic structure and the properties of solids*: Freeman, San Francisco.

Ho, J. K., Jong, C. S., Chiu, C. C., Huang, C. N., Chen, C. Y., & Shih, K. K. (1999). *Appl. Phys. Lett.* **74**, 1275 and references therein.

Hu, Z., Golden, M. S., Fink, J., Kaindl, G., Warda, S. A., Reinen, D., Mahadevan, P., & Sarma, D. D. (2000). *Phys. Rev*. B**61**, 3739 and references therein.

Jain, S. C., Willander, M., Narayan, J. & Van Overstraeten, R. (2000). *J. Appl. Phys.* **87**, 965.

Lin, M. E., Ma, Z., Huang, F. Y., Fan, Z. F., Allen, L. H. & Morkoc, H. (1994). *Appl*. *Phys. Lett* **64**, 1003.

Maeda, T., Yasuo Koide & Murakami, M. (1999). *Appl. Phys. Lett*. **75**, 4145.

Pearton, S. J., Zolper, J. C., Shul, R. J. & Ren, F. (1999). *J. Appl. Phys*. **86**, 1.

Srivastava, P., Haack, N., Wende, H, Chauvistre, R. & Baberschke, K. (1997). *Phys. Rev.*B**56**, R4398.

 Received 31 July 2000 • Accepted 24 January 2001