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Electronic structure of oxidized Ni/Au contacts on *p*-GaN investigated by x-ray absorption spectroscopy

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X-ray absorption spectroscopy has been used to investigate the electronic structure of as-deposited and oxidized Ni/Au contacts on *p*-GaN. The Ni *K*-, $L_{2,3}$ -, and O *K*-edges x-ray absorption spectra clearly show the formation of NiO in the annealed contacts. Annealing in air increases Ni-site hole concentration and slightly shortens the nearest-neighbor Ni–O bond length, which enhances *p*–*d* hybridization and charge transfer from Ni to O. The observed very low specific contact resistance in the oxidized contacts is found to be due to the enhanced hole concentration at the Ni site.

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The metal–semiconductor contact is a crucial interface structure that determines the characteristics of optoelectronic and microelectronic devices. The selection of metal contacts requires proper understanding of their electronic structures.¹ Several combinations of metals were tested for the contacts for *n*- and *p*-type GaN.^{2,3} The most widely used ohmic contacts for *n*-type GaN are based on an Al/Ti bilayer.⁴ Finding a suitable ohmic contact for *p*-GaN has been a major problem. Recently, Ho *et al.* oxidized the Ni/Au-bilayer contact on *p*-GaN and obtained a very low specific contact resistance of $1 \times 10^{-6} \Omega \text{ cm}^2$.⁵ This finding prompted intensive investigations on the Ni/Au contacts.⁶ Ho *et al.* proposed that during annealing of the Ni/Au contacts in air, Ni atoms diffuse to the surface and were oxidized to form a crystalline NiO layer. They attributed the low-resistance ohmic contact to the formation of *p*-NiO most likely with Ni in the 3+ state or with the presence of interstitial oxygen.^{5,6} To understand these proposed properties, we carry out Ni *K*-, $L_{2,3}$ -, and O *K*-edge x-ray absorption spectroscopic investigation of the electronic structures of the as-deposited and oxidized Ni/Au contacts on *p*-GaN.

X-ray absorption spectra were measured using the facility at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan, operating with an electron energy of 1.5 GeV and a maximum stored current of 200 mA. For all samples, the Ni *K*-edge absorption spectra were obtained

from wiggler beamline by the fluorescence yield method, while the Ni $L_{2,3}$ -edges and O *K*-edge spectra were obtained from high-energy spherical grating monochromator and Dragon beamlines by the sample drain current method in a vacuum better than 10^{-9} Torr. The spectra of the reference samples, namely the Ni foil and NiO thin film, were also recorded. The GaN samples used in this study were grown by a low-pressure metalorganic chemical vapor deposition method on the sapphire (0001) substrates. Details of the preparation and characterization of these samples are given elsewhere.⁵ We have selected one as-deposited *p*-GaN/Ni(100 Å)/Au(50 Å) and two oxidized (a) *p*-GaN/Ni(50 Å)/Au(50 Å) and (b) *p*-GaN/Ni(100 Å)/Au(50 Å) samples. Annealing was done in air at 500 °C. The Au layers in all these samples have the same thickness. Since Ho *et al.* reported that the annealed samples with a Ni thickness of 50 Å yielded a much lower contact resistance than those with a Ni-layer thickness of 100 Å, we selected samples with Ni-layer thicknesses of 50 and 100 Å, respectively, in order to understand the thickness dependence.

Figure 1 shows the normalized Ni *K*-edge x-ray absorption near edge structure (XANES) spectra of the as-deposited and oxidized *p*-GaN/Ni/Au samples measured in the fluorescence mode at room temperature. As seen in the inset of Fig. 1, the spectral features of the as-deposited sample resemble those of the Ni foil, which shows that the Ni layer deposited on *p*-GaN is a metallic layer and there is no trace of NiO. The spectral features of the oxidized samples in Fig. 1 are very similar to those of NiO, except the absence of the minor

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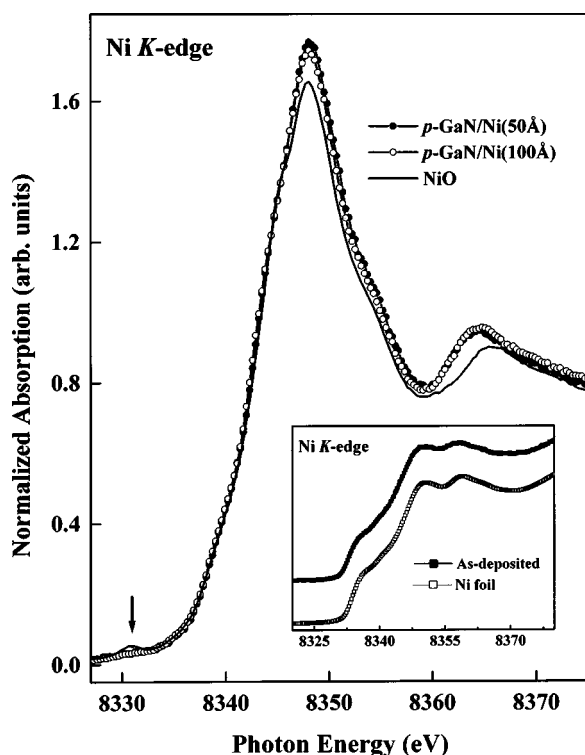


FIG. 1. Normalized Ni K -edge x-ray absorption spectra of the as-deposited and oxidized Ni/Au contacts on p -GaN and the Ni foil and NiO thin film.

pre-edge peak (marked by a vertical arrow). The similarity of the spectral features is an evidence of the formation of NiO after annealing at 500 °C in air, which is consistent with the previous report.⁶ In Fig. 1, the main peaks in the spectra of the annealed samples do not show any significant shift with respect to that of the NiO thin film indicating that Ni is in the divalent state. One would expect considerable shift of the peak positions in the XANES spectra if Ni³⁺ ions were present in the contacts.⁷ Thus, the spectra indicate that Ni³⁺ ions are not significantly present in these oxidized samples, which does not support the existence of Ni³⁺ ions proposed by Ho *et al.* According to Fig. 1, the absorption intensity at and above the main edge is significantly larger for the annealed samples than that for NiO and the intensity of the main feature is slightly larger for p -GaN/Ni(50 Å)/Au(50 Å) than for p -GaN/Ni(100 Å)/Au(50 Å). An enhancement of the Ni K near edge intensity corresponds to the increase of the number of unoccupied Ni $4p$ -derived states, which implies a reduction of the number of occupied Ni $4p$ -derived states and a loss of Ni $4p$ -orbital charge upon annealing.

Figure 2 shows the O K -edge XANES spectra of the annealed samples and NiO. The as-deposited sample does not yield any O K -edge signal implying that there is no NiO in the metal contact. The spectra are normalized to have the same area in the energy range between 550 and 570 eV (not fully shown in the figure). The O K -edge XANES spectra reflect transitions to the unoccupied O $2p$ -derived states. The hybridization with the relatively narrow $3d$ and broader $4sp$ Ni bands results in features A and B in the spectra.⁸ The area of feature A was determined by subtracting a Gaussian type background from the measured spectra as shown by the dotted lines in Fig. 2. The area under feature A in the spectra of

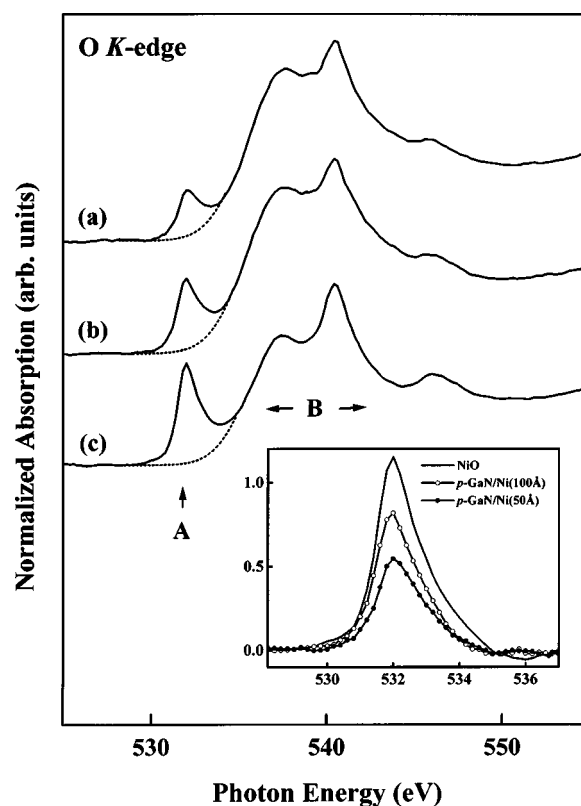


FIG. 2. Normalized O K -edge x-ray absorption spectra of (a) p -GaN/Ni(50 Å)/Au(50 Å), (b) p -GaN/Ni(100 Å)/Au(50 Å), and (c) NiO thin-film samples. The inset shows the area of feature A of the three samples.

the oxidized p -GaN/Ni/Au samples decreases with respect to that of the NiO thin film. This clearly indicates that there is a decrease in the density of the unoccupied states of $2p$ character due to strong hybridization between Ni $3d$ and O $2p$ states after annealing. The p -GaN/Ni(50 Å)/Au(50 Å) sample has the smallest area and the largest p - d hybridization among the samples studied.

The Ni $L_{2,3}$ -edges XANES spectra gives information on the Ni-site electronic structure. The area under the white line feature is directly related to the Ni-site hole concentration.^{9,10} Figure 3 shows the normalized Ni $L_{2,3}$ -edges x-ray absorption spectra. The area under the white line feature was extracted relative to the fitted arctangent function of the continuum step centered at the maximum height. The integrated area from 850 to 863 eV is found to be significantly larger for the oxidized samples than for NiO. The inset in the figure shows the relationship between the area under the Ni L_3 edge and the specific contact resistance for the samples investigated. The annealed samples have a much lower resistance and a larger white-line-feature area than the NiO thin film (NiO is an insulator and has a resistance in the order of $\sim 10^{13} \Omega \text{ cm}^2$).¹¹ The oxidized Ni (50 Å) sample has the largest Ni L_3 -edge peak area. The trend of the white-line-feature areas is similar to that of Ni K edge. Both Ni K - and L_3 -edge results show the formation of the p -NiO layer in the contact after annealing in air. The Ni L_3 -edge result shows that the increase of the Ni-site hole concentration is responsible for the low specific contact resistance.

Figure 4 shows the Fourier transform (FT) amplitudes of the extended x-ray absorption fine structure (EXAFS) $k^3 \chi$

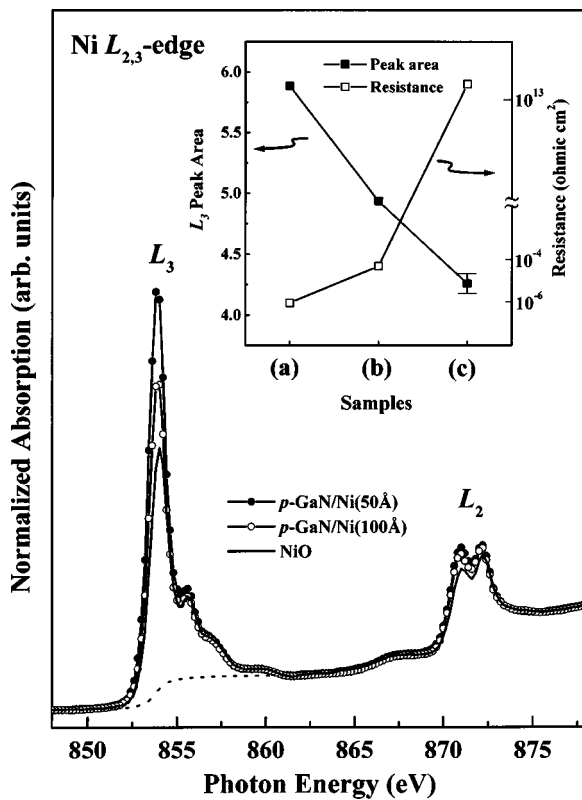


FIG. 3. Normalized Ni $L_{2,3}$ -edges x-ray absorption spectra of (a) p -GaN/Ni(50 Å)/Au(50 Å), (b) p -GaN/Ni(100 Å)/Au(50 Å), and (c) NiO thin-film samples. The inset qualitatively represents the correlation between contact resistance and the Ni L_3 peak area of the three samples. Note that the axis is broken to show the high resistance of NiO thin films.

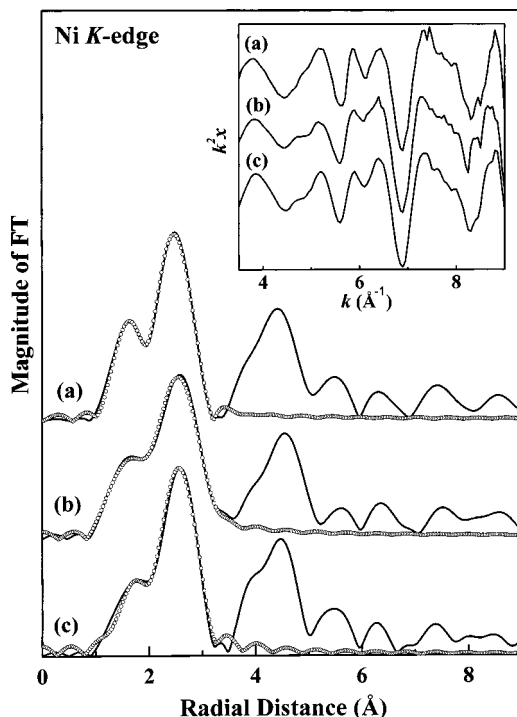


FIG. 4. Fourier transform amplitudes of the EXAFS $k^3 \chi$ data at the Ni K edge from $k = 3.5$ to 9 \AA^{-1} (solid line) for (a) p -GaN/Ni(50 Å)/Au(50 Å), (b) p -GaN/Ni(100 Å)/Au(50 Å), and (c) the NiO thin films. Final fits of the theory to nearest-neighbor Ni–O and Ni–Ni bond lengths are shown by the open circles. The inset represents the Ni K -edge EXAFS oscillations $k^2 \chi$ data.

data at the Ni K edge for the oxidized samples and the reference NiO. The inset represents the Ni K -edge EXAFS oscillations $k^2 \chi$ data. Our result shows that the local atomic structure in the oxidized samples closely resemble that in NiO. The first peaks of the FT curves (marked by the vertical arrow) correspond to the nearest-neighbor (NN) Ni–O bond length.¹² Our analysis involved the use of the multiple-scattering EXAFS computer program FEFF6,¹³ and the non-linear least-squares-fitting computer program FEFFIT.¹⁴ As shown in Fig. 4, the quality of the fit for the NN Ni–O and Ni–Ni are quite good. We obtained NN Ni–O (Ni–Ni) bond lengths of 1.91 ± 0.02 (2.91 ± 0.03), 1.95 ± 0.02 (2.99 ± 0.03), and 2.03 ± 0.02 (2.97 ± 0.03) Å for p -GaN/Ni(50 Å)/Au(50 Å), p -GaN/Ni(100 Å)/Au(50 Å), and the NiO thin film, respectively. The NN Ni–O bond length for p -GaN/Ni(50 Å)/Au(50 Å) shifts slightly toward the lower R relative to those for p -GaN/Ni(100 Å)/Au(50 Å) and NiO. The p - d hybridization is generally believed to depend on the energy separation between the Ni $3d$ and O $2p$ states and the NN Ni–O bond length. The absolute square of the hybridization coupling constant, $|V_{pd}|^2$, is qualitatively proportional to (r_d^3/d_{NN}^7) , where r_d and d_{NN} are the transition metal d -orbital radius and the $3d$ transition metal–NN bond length, respectively.¹⁵ Thus, the decrease in the NN Ni–O bond length may enhance the O p -Ni d hybridization, which can be correlated with the low contact barrier between p -NiO and p -GaN.

In summary, we find that the low contact resistance is attributable to the increase in the Ni-site hole concentration and the change in the NN Ni–O bond length.

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