Synchrotron radiation photoemission analysis for $(NH_4)_2S_x$-treated GaAs

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The chemistry of the $(NH_4)_2S_x$-treated *n*-GaAs (100) surfaces has been studied using synchrotron radiation photoemission spectroscopy. Ga 3*d*, As 3*d*, and S 2*p* photoemission spectra are measured before and after annealing in vacuum with a photon energy of about 210 eV, where S 2*p* core level spectra can be sensitively detected. It is found that Ga-S, As-S, and S-S bonds are formed on the as-treated GaAs surfaces, and that stable Ga-S bonds become dominant after annealing at 360 °C for 10 min in vacuum. The thickness of the surface sulfide layer is reduced from about 0.5 to 0.3 nm by annealing. The surface Fermi-level position of the as-treated surfaces is determined to be about 0.8 eV below the conduction band minimum, which is about 0.1 eV closer to the valence band maximum than that of the untreated surfaces. A Fermi-level shift of 0.3 eV toward a flat band condition is also observed after annealing. It is found that the Ga-S bonding plays an important role in passivating GaAs surfaces.

I. INTRODUCTION

The problem of GaAs surface Fermi level pinning has been one of the most important subjects to both surface sciences and semiconductor device fabrication. Intense work has been done to understand the Fermi level pinning mechanism.[1-4] However, it is difficult to reduce the GaAs surface state density and to actually control the GaAs surface Fermi level position. In recent years attempts have been made to passivate the GaAs surfaces by sulfide treatment with Na_2S,[5-8] $(NH_4)_2S$,[9] and $(NH_4)_2S_x$.[10-13] It has been reported that the Schottky barrier heights of the diodes formed on the $(NH_4)_2S_x$-treated GaAs are strongly dependent on the metal work function,[11,12] which suggests that the $(NH_4)_2S_x$ treatment can effectively reduce the surface state density. However, the mechanism by which the GaAs surfaces are passivated using $(NH_4)_2S_x$ solution has not been clearly understood. A model has been proposed[14] to explain the difference in the treatment effect among those sulfides mentioned above, in which Ga-S bonds were assumed to play the most important role. However, Sandroff *et al.* reported that only As-S bonds were observed under their experimental conditions. Although Spindt *et al.*[15] found that Ga-S bonds exist on the $(NH_4)_2S_x$-treated GaAs surfaces using synchrotron radiation photoemission spectroscopy (SRPES) where $h\nu = 80$ and 100 eV, no information on the core levels of the S atoms has been reported. It is difficult to analyze the bonding states of surface sulfur atoms using conventional x-ray photoelectron spectroscopy (XPS) with Mg*Kα* (1253.6 eV) or Al*Kα* (1486.6 eV) characteristic x rays, because the escape depth of the S 2*p* core electrons is almost 2 nm and the photoionization cross section is relatively small. Therefore, a surface sensitive photoelectron signal with a high S/N ratio is difficult to be taken by conventional XPS measurement. To solve this problem, the authors adjusted the photon energy to about 210 eV, which is the condition for minimum escape depth and is about 20 times as large as a photoionization cross section for Al*Kα* with S 2*p*. In this paper, the chemistry and the band bending of the $(NH_4)_2S_x$-treated GaAs surfaces are discussed.

II. EXPERIMENT

Experiments were performed at BL-1A in the Photon Factory of the National Laboratory for High Energy Physics. The photon energy was adjusted to about 210 eV by using 600 g/mm grating with an incidence angle α of 84° in the grating/crystal monochromator.[16] After the chemical cleaning by HCl, Si-doped *n*-GaAs (100) wafers with a carrier density of 1×10^{18} cm^{-3} were dipped into an $(NH_4)_2S_x$ solution, which was kept at 60 °C, for 1 h. After taking them out of the $(NH_4)_2S_x$ into air, they were blown dry with dry N_2 gas and were loaded into a combined surface analysis system,[17] whose base pressure was less than 1×10^{-7} Pa. The as-treated GaAs wafers have diffused surfaces, because they are covered with a thick sulfur layer. However, the excess sulfur atoms are immediately sublimated and the surfaces become mirrorlike, when the samples are loaded in a vacuum chamber. Synchrotron radiation photoemission spectra of Ga 3*d*, As 3*d*, and S 2*p* core levels were measured before and after annealing at 360 °C for 10 min in vacuum, where the 2×1 RHEED pattern is observed.[18,19] The XPS measurement with Mg*Kα* was also carried out for these samples to confirm the SR photoemission spectra and to see whether or not oxygen atoms exist on the surfaces.

III. RESULTS AND DISCUSSION

The Ga 3*d* photoemission spectra for the *n*-GaAs (100) surfaces with various treatments are shown in Fig. 1(a). Almost no gallium oxide peaks are observed for the $(NH_4)_2S_x$-treated GaAs, whereas HCl-treated and Na_2S-treated samples have noticeable ones. The O 1*s* x-ray pho-

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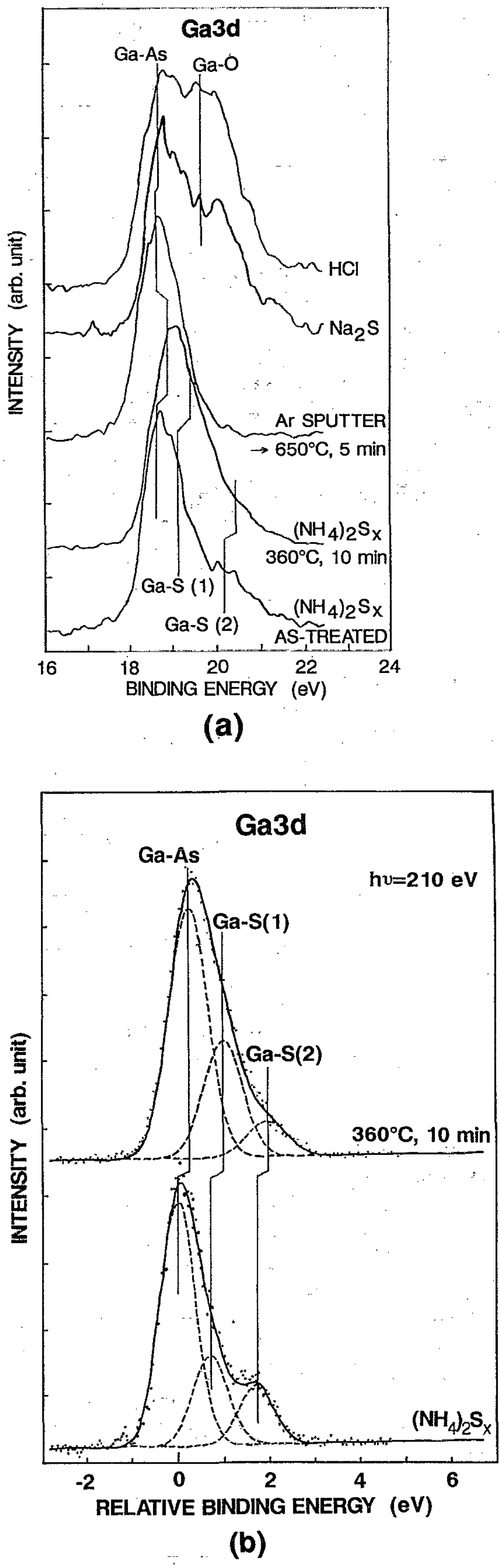


(a)

(b)

FIG. 1. Ga 3*d* photoemission spectra for the *n*-GaAs (100) surfaces with various treatments. (a) the measured spectra and (b) the deconvoluted spectra for the $(NH_4)_2S_x$-treated *n*-GaAs before and after annealing at 360 °C for 10 min in vacuum, where the dots indicate the measured data.

toelectron spectra also revealed that only a slight amount of oxygen exists on the as-treated surfaces. We think that the native oxide is etched by the $(NH_4)_2S_x$ solution, and that the remaining or residual sulfur atoms may protect the surface from oxidation in the air. For the $(NH_4)_2S_x$-treated GaAs, a clear shoulder peak is observed at 1.7 eV higher binding energy than the Ga-As main peak with a good reproducibility. Since the amount of the peak shift for the as-treated surfaces is much larger than that for Ga_2O_3, namely about 1.0 eV, this shifted peak is not due to Ga-O bonds. Spindt *et al.*[15] reported the Ga 3*d* spectra taken with a photon energy of 80 eV, where the Ga 3*d* shoulder peak appeared at 0.55 eV higher binding energy which is assigned to be Ga-S bonds. We think that the difference in the amount of the peak shift is due to the ammonium sulfide solution itself and/or the treatment process. They used $(NH_4)_2S$ solution at room temperature for 10 min, while we used $(NH_4)_2S_x$ solution, which contains more excess sulfur molecules, at 60 °C for 60 min. The etching rate of GaAs is larger for the $(NH_4)_2S_x$ solution than for the $(NH_4)_2S$ solution. The more excess sulfur atoms at higher temperature might enhance the formation of another Ga-S bonding. Since the HCl pre-cleaning process was employed in our experiment, there is a possibility that the GaAs surface was Cl-contaminated. However, no Cl peak was observed for the $(NH_4)_2S_x$-treated GaAs surfaces. Moreover, almost the same spectra were obtained for the $(NH_4)_2S_x$-treated GaAs without HCl pre-cleaning. Therefore, we assign the 1.7-eV-shifted shoulder peak as an another Ga-S bonding, namely Ga-S(2). In order to distinguish this peak from the reported one with a 0.55-eV shift, we call the previously reported peak as Ga-S(1) in this report.

By using both the Ga-S(1) and the Ga-S(2) peaks, which have the same FWHM as for the heat-cleaned GaAs, we deconvoluted the Ga 3*d* spectra, as shown in Fig. 1(b). Since a good fitting curve is obtained by the convolution of these two shifted peaks and the Ga-As main peak, it can be said that two kinds of Ga-S chemical bonds exist on the $(NH_4)_2S_x$-treated GaAs surfaces. The peak intensity ratio of Ga-S(1) to Ga-S(2) increases after annealing at 360 °C, which is in fairly good agreement with the ratio of S-Ga(1) to S-Ga(2) in S 2*p* spectra, as described later. This suggests that the Ga-S(1) is more stable than the Ga-S(2). Ga-S(1) and Ga-S(2) are assumed to be Ga_2S or GaS, and Ga_2S_3, respectively, because a small charge transfer from Ga to S per unit Ga atom causes a small chemical shift.

As shown in Fig. 1(a), the Ga 3*d* binding energy for the as-treated GaAs surfaces is lower than that for the HCl-cleaned surfaces, which may suggest the upward band bending due to the reduction of As_{Ga} antisite defects[20] by the $(NH_4)_2S_x$ treatment. The Ga 3*d* main peak for the Ga-As bonds, however, shifted 0.3 eV toward a higher binding energy by annealing at 360 °C in vacuum. The same peak shift as Ga 3*d* was also observed for As 3*d* and S 2*p* spectra, indicating that a Fermi level shift of 0.3 eV toward a flat band condition occurs by annealing. The mechanism of the decrease in the upward band bending is

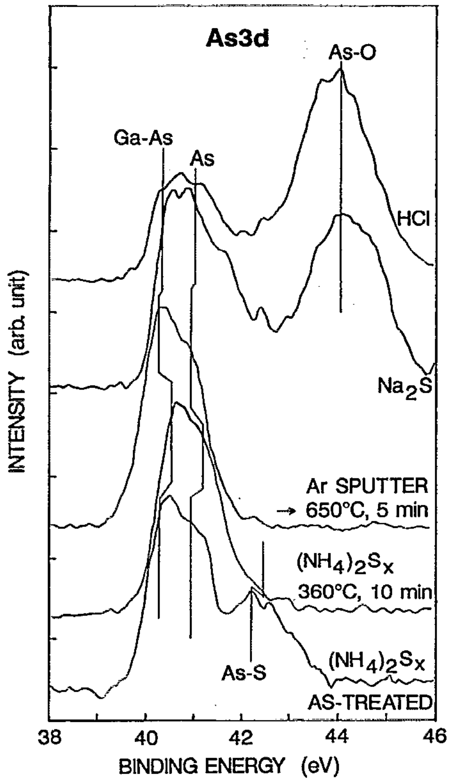


FIG. 2. As 3*d* photoemission spectra for the *n*-GaAs (100) surfaces with various treatments.

not clearly understood at present. Unfortunately we have no *in situ* photoluminescence data for the annealed surfaces, so whether the annealed surfaces maintain the "passivated" surfaces or not is also unclear. Further investigation is necessary to clarify the annealing behavior of the $(NH_4)_2S_x$-treated GaAs.

The As 3*d* photoemission spectra for the *n*-GaAs surfaces with various treatments are shown in Fig. 2. A large shifted peak, which can be assigned for As_2O_3, is observed for HCl-treated and Na_2S-treated surfaces, whereas no arsenic oxide peaks are detected for the $(NH_4)_2S_x$-treated GaAs. As-S bonds with about a 2.0-eV peak shift are observed for the as-treated GaAs surfaces. This peak shift is very close to that reported by Spindt *et al.*[15] Although it is difficult to determine the bonding state of As-S, this state might be due to the As_4S_4-like bonds,[21] rather than the As_2S_3-like bonds, judging from the small peak shift of 2.0 eV. The 0.7-eV shift of the As 3*d* shoulder peak is thought to be due to the spin-orbit splitting and the elemental As atoms.[22] The As-S peak almost disappears after annealing at 360 °C, suggesting that As-S bonds are less stable than Ga-S bonds. The total energy of the system is expected to be reduced by the formation of Ga-S terminated surfaces. An As-Ga main peak shift of 0.3 eV toward a flat band condition is also observed for the As 3*d* spectra after annealing. Therefore, this shift is due to the decrease in the band bending, as mentioned above.

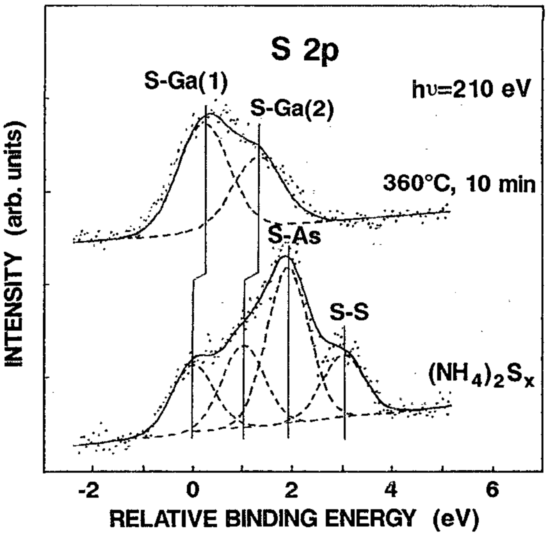
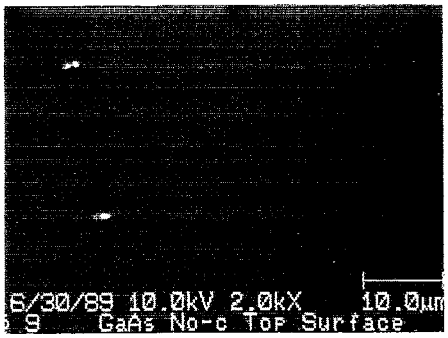
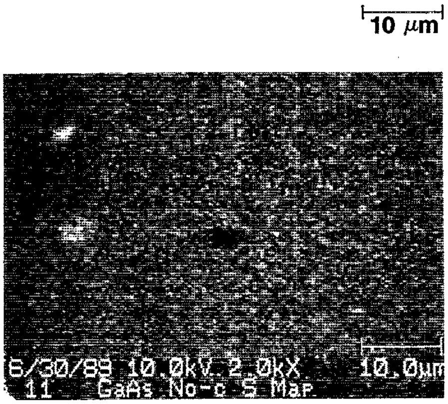


FIG. 3. S 2*p* photoemission spectra for the $(NH_4)_2S_x$-treated *n*-GaAs (100) surfaces before and after annealing at 360 °C for 10 min in vacuum. The broken line, the solid line, and the dots indicate the deconvoluted spectra, the total spectra, and the measured data, respectively.

Figure 3 shows the S 2*p* photoemission spectra for the $(NH_4)_2S_x$-treated GaAs. Four peaks are observed for the as-treated GaAs surfaces, and after annealing only two peaks of them are remained. Judging from the results that the intensities of the As-S peak in the As 3*d* spectra and the Ga-S(2) peak in the Ga 3*d* spectra decreased after annealing, two components with lower binding energies for the as-treated surface are due to Ga-S bonds. Although there is a possibility that As-S compounds are desorbed as molecules by annealing, the amount of the sulfur atoms on the surface remained almost unchanged even after annealing. Therefore, we think that the As-S bonds are broken and the S atoms are moved from As to Ga atoms. This identification is also verified by assuming that the amount of the chemical shift depends on the charge transfer. The amount of the charge transfer from Ga to S is considered to be larger than from As to S, because the electronegativity difference between Ga and S is larger than that between As and S.[23] Therefore, these peaks correspond to the Ga-S(1), Ga-S(2), As-S, and S-S bonds in the order of the binding energy. A smaller chemical shift is expected for Ga_2S_3, because the amount of charge transfer per sulfur atom is smaller for Ga_2S_3 than for Ga_2S or GaS. Therefore, Ga-S(1) and (2) are, respectively, thought to be Ga_2S or GaS, and Ga_2S_3, as previously mentioned. It can be seen that the As-S and S-S bonds disappear after annealing at 360 °C. This suggests that these bonds are less stable than Ga-S bonds. After annealing at 360 °C for 10 min, Ga-S bonds become dominant. Though we did not simultaneously observe the surface structure, this rearrangement in the bonding state is thought to be related to the surface reconstruction.[18,19] The thickness of the sulfides on the as-treated GaAs surfaces was determined to be about 0.5 nm by the photoelectron peak intensities, escape depths and photoionization cross sections, assuming a uniform GaS + AsS layer. After annealing, the thickness decreases to about 0.3 nm, which corresponds to about one monolayer.



(a) SECONDARY ELECTRON IMAGE



(b) S_{LVV} AUGER ELECTRON IMAGE

FIG. 4. (a) Secondary electron images and (b) S_{LVV} Auger electron images for the $(NH_4)_2S_x$-treated GaAs surfaces taken by a micro Auger electron spectrometer.

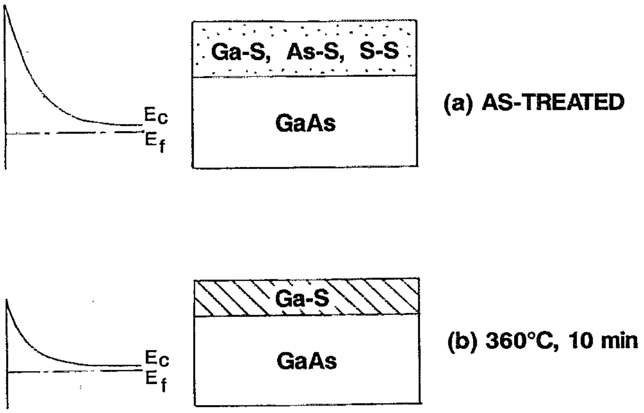


FIG. 5. Schematic diagrams of the $(NH_4)_2S_x$-treated n-GaAs surface chemistry and the band bending (a) before and (b) after annealing at 360 °C for 10 min in vacuum. Ga-S bonds become dominant at 360 °C. The band diagrams show that the upward band bending occurs by the $(NH_4)_2S_x$ treatment, and that the decrease in the band bending of 0.3 eV occurs by annealing.

Figure 4 shows (a) the secondary electron images and (b) the S_{LVV} Auger electron images for the $(NH_4)_2S_x$-treated GaAs surfaces taken by a micro Auger electron spectrometer. As can be seen in Fig. 4, the surface morphology of the $(NH_4)_2S_x$-treated GaAs is smooth and the distribution of the sulfur atoms on the $(NH_4)_2S_x$-treated surfaces is homogeneous. On the other hand, the Na and S atom distribution for the Na_2S-treated GaAs surfaces is inhomogeneous.[24] Similar results were also reported by Besser *et al.*[9] Judging from the surface chemistry and the surface homogeneity, $(NH_4)_2S_x$ solution is superior to Na_2S solution for the GaAs surface passivation.

Based on these results, schematic diagrams of the $(NH_4)_2S_x$-treated n-GaAs (100) surface chemistry and the band bending are shown in Fig. 5. The $(NH_4)_2S_x$-treated GaAs surfaces are covered with a sulfide layer containing Ga-S, As-S, and S-S bonds. Assuming that the surface Fermi level of the heat-cleaned n-GaAs (100) surfaces is located at 0.8 eV below the conduction band minimum (CBM),[25] the surface Fermi level position of the as-treated surfaces was determined to be about 0.8 eV from the CBM, which is about 0.1 eV closer to the valence band maximum than that of the untreated surfaces, as shown in Figs. 1(a) and 2. The surface sulfide thickness is reduced from about 0.5 to 0.3 nm by annealing at 360 °C in vacuum. As-S and S-S bonds are broken and the Ga-S bonds become dominant at this stage. This suggests that Ga-S bonds are more stable than As-S and S-S bonds, which confirms the previous report.[18] The heat of formation for gallium sulfide is higher than that for arsenic sulfide.[26,27] which agrees well with the photoemission data. A surface Fermi level shift of 0.3 eV towards the CBM occurs at 360 °C. This suggests that the surface Fermi level, which is pinned at about 0.8 eV from the CBM for the as-treated surfaces, changes to about 0.5 eV from the CBM by annealing. Although the initial band bending for the as-treated GaAs surfaces can be explained well by assuming that As_{Ga} antisite defect density is reduced by the $(NH_4)_2S_x$ treatment,[20] the annealing behavior is not clearly understood at present. The Ga-S bonding is thought to be the key for passivating GaAs surfaces.

IV. CONCLUSIONS

Ga $3d$, As $3d$, and S $2p$ synchrotron radiation photoemission spectra for the $(NH_4)_2S_x$-treated n-GaAs(100) surfaces were measured to clarify the passivating mechanism of the $(NH_4)_2S_x$ treatment. It was found that Ga-S, As-S, and S-S bonds exist on the $(NH_4)_2S_x$-treated GaAs surfaces, and that the Ga-S bonds become dominant after annealing at 360 °C for 10 min. The initial upward band bending of the as-treated surfaces suggests the reduction of As_{Ga} antisite defects. A surface Fermi level shift of 0.3 eV towards the CBM was observed after annealing. Further investigation is necessary to clarify the mechanism of the decrease in the band bending for the annealed surfaces. It can be concluded that the Ga-S bonding is the key to passivate GaAs surfaces.

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[1] W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. **16**, 1422 (1979).

[2] W. E. Spicer, Z. Liliental-Weber, E. Weber, N. Newman, T. Kendelewicz, R. Cao, C. McCants, P. Mahowald, K. Miyano, and I. Lindau, J. Vac. Sci. Technol. B **6**, 1245 (1988).

[3] J. M. Woodall and J. L. Freeouf, J. Vac. Sci. Technol. **19**, 794 (1981).

[4] H. Hasegawa and H. Ohno, J. Vac. Sci. Technol. B **4**, 1130 (1986).

[5] C. J. Sandroff, R. N. Nottenburg, J.-C. Bischoff, and R. Bhat, Appl. Phys. Lett. **51**, 33 (1987).

[6] R. S. Besser and C. R. Helms, Appl. Phys. Lett. **52**, 1707 (1988).

[7] C. J. Sandroff, M. S. Hedge, L. A. Farrow, C. C. Chang, and J. P. Harbison, Appl. Phys. Lett. **54**, 362 (1989).

[8] C. J. Spindt, R. S. Besser, R. Cao, K. Miyano, C. R. Helms, and W. E. Spicer, Appl. Phys. Lett. **54**, 1148 (1989).

[9] R. S. Besser and C. R. Helms, J. Appl. Phys. **65**, 4306 (1989).

[10] J. Fan, H. Oigawa, and Y. Nannichi, Jpn. J. Appl. Phys. **27**, L1331 (1988).

[11] H. Oigawa, J. Fan, Y. Nannichi, K. Ando, K. Saiki, and A. Koma, *Extended Abstracts of the 20th Conference on Solid State Devices and Materials* (The Japan Society of Applied Physics, Tokyo, 1988), p. 263.

[12] J. Fan, H. Oigawa, and Y. Nannichi, Jpn. J. Appl. Phys. **27**, L2125 (1988).

[13] H. Sugahara, M. Oshima, H. Oigawa, H. Shigekawa, and Y. Nannichi, *Extended Abstracts of the 21st Conference on Solid State Devices and Materials* (The Japan Society of Applied Physics, Tokyo, 1989), p. 547.

[14] Y. Nannichi, J. Fan, H. Oigawa, and A. Koma, Jpn. J. Appl. Phys. **27**, L2367 (1988).

[15] C. J. Spindt, D. Liu, K. Miyano, P. L. Meissner, T. T. Chiang, T. Kendelewicz, I. Lindau and W. E. Spicer, Appl. Phys. Lett. **55**, 861 (1989).

[16] T. Kawamura, S. Maeyama, M. Oshima, Y. Ishii, and T. Miyahara, Rev. Sci. Instrum. **60**, 1928 (1989).

[17] M. Oshima, T. Kawamura, S. Maeyama, and T. Miyahara, J. Vac. Sci. Technol. A **6**, 1451 (1988).

[18] H. Oigawa, J. Fan, Y. Nannichi, K. Ando, K. Saiki, and A. Koma, Jpn. J. Appl. Phys. **28**, L340 (1989).

[19] H. Hirayama, Y. Matsumoto, H. Oigawa, and Y. Nannichi, Appl. Phys. Lett. **54**, 2565 (1989).

[20] C. J. Spindt and W. E. Spicer, Appl. Phys. Lett. **55**, 1653 (1989).

[21] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer, Minnesota, 1978).

[22] P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. B **18**, 2792 (1978).

[23] L. Pauling, *The Nature of The Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, 1960), p. 93.

[24] H. Sugahara and M. Oshima (unpublished).

[25] N. Newman, W. E. Spicer, T. Kendelewicz, and I. Lindau, J. Vac. Sci. Technol. B **4**, 931 (1986).

[26] R. C. Weast, Ed., *Handbook of Chemistry and Physics*, 65th ed. (CRC Press, Boca Raton, 1984).

[27] O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th ed. (Pergamon Press, Oxford, 1979).