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Annealing behaviors of vacancy-type defects near interfaces between metal contacts and GaN probed using a monoenergetic positron beam

Akira Uedono,[1,a)] Tatsuya Fujishima,[2] Daniel Piedra,[2] Nakaaki Yoshihara,[1] Shoji Ishibashi,[3] Masatomo Sumiya,[4] Oleg Laboutin,[5] Wayne Johnson,[5] and Tomás Palacios[2]

[1]*Division of Applied Physics, Faculty of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan*
[2]*Microsystems Technology Laboratories, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, USA*
[3]*Nanosystem Research Institute "RICS," National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan*
[4]*Wide Bandgap Material Group, National Institute for Materials Science, Tsukuba 305-0044, Japan*
[5]*IQE, 200 John Hancock Road, Taunton, Massachusetts 01581, USA*

Vacancy-type defects near interfaces between metal contacts and GaN grown on Si substrates by metal organic chemical vapor deposition have been studied using a monoenergetic positron beam. Measurements of Doppler broadening spectra of the annihilation radiation for Ti-deposited GaN showed that optically active vacancy-type defects were introduced below the Ti/GaN interface after annealing at 800 °C. Charge transition of those defects due to electron capture was observed and was found to correlate with a yellow band in the photoluminescence spectrum. The major defect species was identified as vacancy clusters such as three to five Ga-vacancies coupled with multiple nitrogen-vacancies. The annealing behaviors of vacancy-type defects in Ti-, Ni-, and Pt-deposited GaN were also examined. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4892834]

GaN-based electronic devices, such as AlGaN/GaN high electron mobility transistors (HEMTs) and heterojunction bipolar transistors (HBTs), have attracted substantial attention for use in high-temperature, high-power, and high-frequency applications.[1,2] Their potential is mainly attributed to the physical properties of GaN and AlGaN, such as large band-gaps, great electron mobility, and high breakdown voltages. Developments in the fabrication technology of GaN-HEMTs and HBTs have made them capable of low on-resistance and high output power, which are essential for high-performance power switching and microwave devices. With increasing demands for high-temperature and high-power operations, however, detailed understanding of the failure mechanisms of these devices—such as the creation of trap centers in AlGaN and dielectric breakdown—have become important issues. The degradation of metal contacts is also a major factor that reduces device reliability.[3] The formation of Schottky and ohmic contacts for GaN-devices requires highly tailored recipes using multi-layer metallization, such as Ni/Au, Pt/Au, and Ti/Al/Ni/Au. With increasing junction temperature, atomic diffusion between metal contacts and AlGaN/GaN could occur and causes a shift in the Schottky barrier height or an increase in the ohmic contact resistance which would introduce parasitic resistance. Atomic diffusion within the metal layers could also affect the electrical properties of the devices. Thus, detailed knowledge regarding point defects and their reaction near the metal/semiconductor interface is crucial. Positron annihilation is a powerful technique for evaluating vacancy-type defects in semiconductors and metals.[4] In the present study, we have used a monoenergetic positron beam to study the annealing behaviors of vacancy-type defects near the interface between metal contacts (Ti, Ni, and Pt) and GaN grown on a Si substrate by metal organic chemical vapor deposition (MOCVD).

When a positron is implanted into condensed matter, it annihilates with an electron and emits two 511-keV γ quanta.[4] The energy distribution of the annihilation γ rays is broadened by the momentum component of the annihilating electron-positron pair p_L, which is parallel to the emitting direction of the γ rays. The energy of the γ rays is given by $E_\gamma = 511 \pm \Delta E_\gamma$ keV. The Doppler shift ΔE_γ is given by $\Delta E_\gamma = p_L c/2$, where c is the speed of light. A freely diffusing positron may be localized in a vacancy-type defect because of Coulomb repulsion from positively charged ion cores. Because the momentum distribution of the electrons in such defects differs from that of electrons in the bulk material, these defects can be detected by measuring the Doppler broadening spectra of the annihilation radiation. The resultant changes in the spectra are characterized by the S parameter, which mainly reflects changes due to the annihilation of positron-electron pairs with a low-momentum distribution, and by the W parameter, which mainly characterizes changes due to the annihilation of pairs with a high-momentum distribution. In general, the characteristic value of S (W) for the annihilation of positrons trapped by vacancy-type defects is larger (smaller) than that for positrons annihilated from the free-state. For group-III nitrides, because an isolated nitrogen vacancy (V_N) is positively charged, the major trapping center of positrons is Ga vacancies (V_{Ga}) and their complexes.[4]

The samples investigated were 1-μm-thick unintentionally doped (semi-insulating) GaN layers grown on Si(111) substrates by MOCVD. Before deposition of the GaN layer, an AlGaN(70 nm)/AlN(100 nm)-nucleation layer was

a)uedono.akira.gb@u.tsukuba.ac.jp

deposited on the Si substrate at about $1100\,^\circ$C, and then a 2.3-μm-thick AlN/GaN superlattice structure was deposited on the AlGaN/AlN/Si. The major impurities of the GaN layer were C and O, and their concentrations were $2 \times 10^{17}/cm^{-3}$ and $4 \times 10^{16}/cm^{-3}$, respectively. The growth method of the samples and the electrical properties of transistors formed on the templates prepared by a similar technique are described elsewhere.[5] 20-nm-thick Ti, Ni, and Pt layers were deposited on different samples using an electron beam evaporator. After the deposition, the samples were annealed up to $800\,^\circ$C in N_2-atmosphere using a rapid thermal annealing system (1 min). The metal layers were then removed by wet etching. No detectable defects were introduced by the etching process. Photoluminescence (PL) spectra were measured using a 325-nm He-Cd laser as an excitation source and a Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer. All measurements were made at room temperature under the same condition.

With a monoenergetic positron beam, Doppler broadening spectra of the annihilation radiation were measured with a Ge detector as a function of the incident positron energy E. The spectra were characterized by the S parameter, defined as the fraction of annihilation events over the energy range of 510.24–511.76 keV, and by the W parameter, defined as the annihilation events in the ranges of 504.20–507.60 keV and 514.40–517.80 keV. Doppler broadening profiles were also measured using a coincidence system. The relationship between S and E was analyzed by VEPFIT, a computer program developed by van Veen *et al.*[6] The measurements of the Doppler broadening profile were done in the dark and under the illumination of a 325-nm HeCd-laser (KIMMON KOHA, IK3802R-G). The relationship between the S value and the photon energy was measured using a spectrometer with a Xe-lamp. Doppler broadening spectra were calculated with our QMAS computational code, which uses the projector augmented-wave (PAW) method, for the systems containing defects. Details of the calculation method are described elsewhere.[7] The S and W values were calculated from the simulated spectra for the defect-free case and typical vacancies such as V_{Ga} and $(V_{Ga})_n(V_N)_m$ (n, m = 1, 2,...). The (S,W) values for complexes between V_{Ga} and carbon, which substitutes Ga-sites or N-sites [$V_{Ga}(C_{Ga})_3$ and $V_{Ga}(C_N)_3$], and those between V_{Ga} and oxygen [$V_{Ga}(O_N)_3$] were also calculated.[7]

Figure 1 shows the S values as a function of incident positron energy E for Ti-deposited GaN before (as-deposited) and after annealing at $800\,^\circ$C. The measurements were done in the dark and under the illumination of HeCd-laser light. All measurements were made after the removal of the Ti layers. The mean implantation depth of positrons is shown on the upper horizontal axis. For the as-deposited sample, the S value increased with decreasing E (<3 keV), which corresponds to the diffusion of positrons toward the surface. In the S–E curve measured in the dark, the S value saturated at $E > 4$ keV and was constant up to 20 keV, suggesting that the characteristic S value for the GaN layer is the value within this energy range (0.4557 ± 0.0001). For GaN grown by hydride vapor phase epitaxy (HVPE), the bulk S value was 0.4466 ± 0.0001, and this value was attributed to the S value for the annihilation of positrons in defect-free GaN.[8]
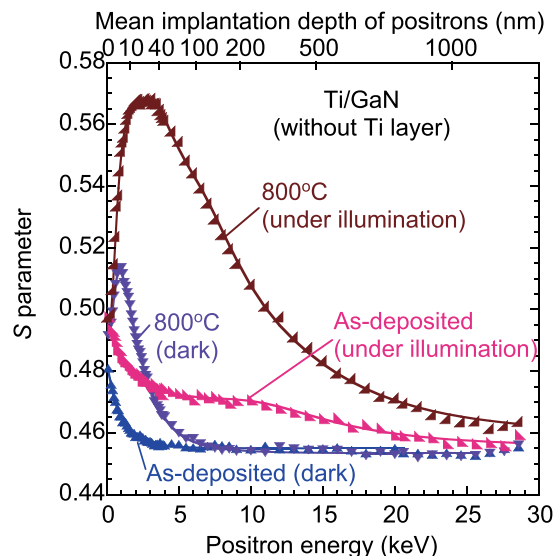

FIG. 1. S parameters as a function of incident positron energy E for Ti-deposited GaN before (as-deposited) and after annealing at $800\,^\circ$C. The measurements were done in the dark (blue and violet symbols) and under the illumination of HeCd-laser light (pink and brown symbols).

Thus, the larger S value observed for the as-deposited sample can be attributed to the annihilation of positrons in vacancy-type defects.

The S value measured at $E < 13$ keV was increased by the illumination. We attribute the observed increase in the S value to an enhancement of the positron trapping by vacancy-type defects under illumination. The transition of the defect charge state from positive (or neutral) to neutral (or negative) increases the trapping probability of positrons.[4] Thus, the electron capture and the charge transition of the vacancy-type defects (V) causing the increase in S can be expressed such as $V^{(+/0)} + e^- \rightarrow V^{(0/-)}$. For the as-deposited sample, the observed S–E curve and the effect of illumination are identical to those for GaN without the metal deposition,[9] suggesting that no detectable defects were introduced by the Ti deposition.

For the annealed sample, the observed increase in the S values at $E \cong 1$ keV (dark) and 3 keV (under illumination) can be attributed to the annihilation of positrons trapped by vacancy-type defects. The S–E curves were analyzed using the VEPFIT code, where the region sampled by the positrons was divided into several blocks. The solid curves in Fig. 1 are fits to the experimental data, and the derived depth distributions of S are shown in Fig. 2. The width of the vacancy-rich region for the annealed sample in the dark is about 5 nm, but under illumination it expands to 220 nm. The presence of the vacancy-rich region can be attributed to atomic diffusion from GaN to the Ti layer, and the resultant introduction of vacancy-type defects. The illumination could introduce the electric field in the GaN layer. Because native vacancies in the GaN layer trap positrons under illumination, the diffusion length of positrons is short. Thus, the effect of the electric field on the positron diffusion is likely to be small.

Figure 3 shows the (S,W) values calculated using the PAW method. The values corresponding to the annihilation of positrons in the delocalized state (defect-free: DF) in GaN and those of positrons trapped by vacancy-type defects,
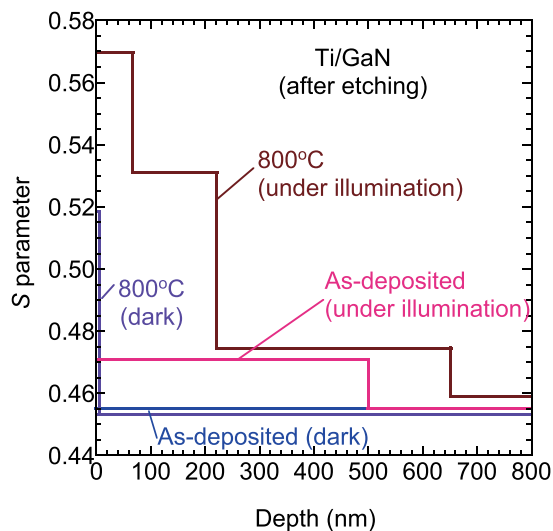
FIG. 2. Depth distributions of S in GaN for Ti-deposited GaN before and after annealing at 800 °C.

$(V_{Ga})_m(V_N)_n$, are shown, where numbers of V_{Ga}s and V_Ns are shown as (m,n). Arrows show the effect of V_Ns coupled with V_{Ga}s, which tends to shift the (S,W) value towards the right-hand side in the $S-W$ plot. In contrast, O_N causes a leftward shift. The (S,W) value for $V_{Ga}(C_{Ga})_3$ is close to that for V_{Ga}, suggesting that the modification of the electron momentum distribution in V_{Ga} due to C_{Ga} is small. The (S,W) values obtained from the coincidence Doppler broadening spectra for Ti-deposited GaN before and after annealing at 800 °C and HVPE-GaN are shown in Fig. 3. The values of E were fixed at 7.1, 2.6, and 30.1 keV for the as-deposited sample, the annealed sample, and HVPE-GaN, respectively. With those incident positron energies, one can get the (S,W) value of the defects in the samples with and without annealing (Fig. 1) and for the annihilation of positions from the free state (for HVPE-GaN). The measurements for Ti-deposited GaN were done under HeCd illumination. The calculated

(S,W) value for DF-GaN was close to that for HVPE-GaN. For the as-deposited GaN, the obtained value lies to the right of the line connecting the calculated values for DF and V_{Ga}, suggesting the major defect species in GaN is vacancy complexes. These defects, however, can typically be detected by positron annihilation without illumination. Thus, considering the major impurities in GaN, the defect species detected by positron annihilation are likely to be related to the complexes between vacancies and carbon impurities or to be vacancy clusters. A detailed discussion regarding the defect identification is provided elsewhere.[9] For the annealed sample, the observed (S,W) value is far from that for V_{Ga} or the complexes between V_{Ga} and V_Ns, but it is close to the (S,W) value for $(V_{Ga})_m(V_N)_n$ (m = 3–5, n = 9,13), suggesting that the defect species introduced by annealing at 800 °C was large vacancy-clusters. Because these vacancy-clusters are optically active ones, carbon atoms are also considered to correlate with them.

Figure 4 shows the S value for Ti-deposited GaN as a function of the photon energy, where the value of E was fixed at 2.5 keV. The PL spectra are also shown in the same figure. Interference fringe patterns observed in the spectra are attributed to the multiple scattering by the surface and interfaces in the samples. For the as-deposited sample, the S value started to increase at a photon energy of 2.71 eV and saturated at 3.23 eV. The observed behavior of S was identical to that for the sample without metal deposition.[9] The energy level of the defects corresponding to the charge transition is therefore considered to be >2.7 eV above the valence band top. For the as-deposited sample, broad luminescence peaks were observed around 2.2 eV and 2.9 eV. The former peak is the so called yellow band (YB) luminescence. The latter peak was observed in the energy range between 2.7 eV and 3.2 eV. This energy range coincides with the one corresponding to the transition of the S value from 0.462 to 0.480. A similar relationship between S and the emission around 2.9 eV was reported for as-deposited GaN.[9] It was also reported that the annealing
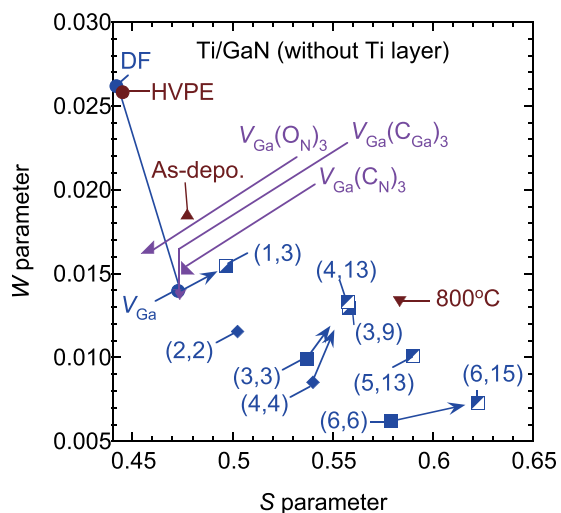

FIG. 3. Relationships between S and W (blue and violet) corresponding to the annihilation of positrons in the delocalized state (defect-free: DF) and that of positrons trapped by $(V_{Ga})_m(V_N)_n$ are shown, where numbers of V_{Ga}s and V_Ns are shown as (m,n). The (S,W) values obtained from the coincidence Doppler broadening spectra for HVPE-GaN and Ti-deposited GaN under illumination are shown in the figure (brown).
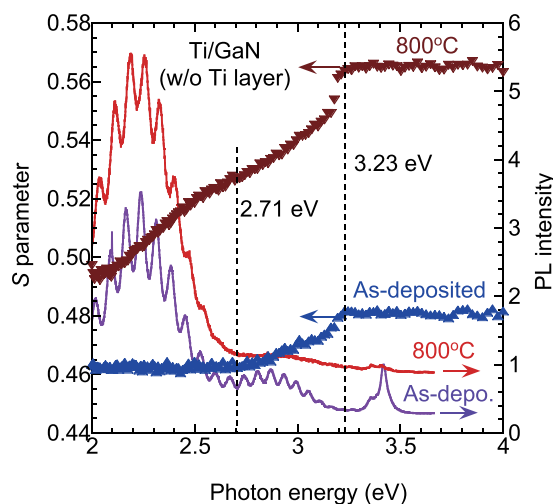

FIG. 4. Relationship between the S value and the photon energy for Ti-deposited GaN before and after annealing at 800 °C. During the measurement, the values of E were set to be 2.6 keV. The PL spectra are also shown, where the spectra were normalized using the peak intensity near band-edge luminescence.
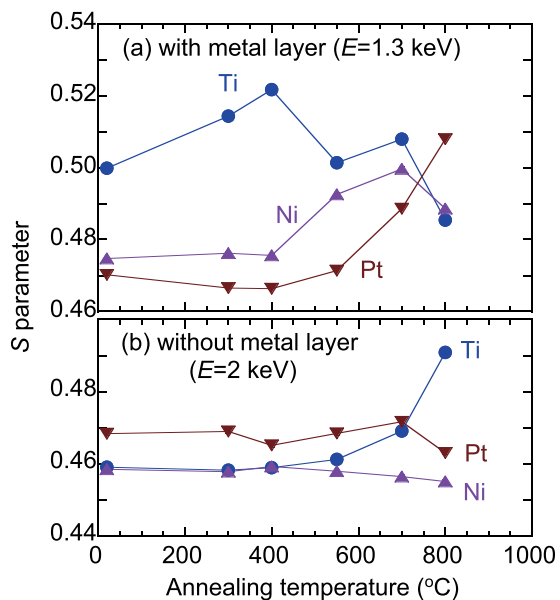
FIG. 5. Annealing behavior of S for Ti-, Ni-, and Pt-deposited GaN before (a) and after the removal of the metal layers (b). All measurements were made in the dark.

behaviors of S and the emission rate around 2.9 eV were close each other. Thus, assuming that the lattice relaxation energy of the defects (Franck-Condon shift) is small and the transitions occur only at the ground states, the origin of the broad PL peak around 2.9 eV can be attributed to the vacancy-type defects detected by positron annihilation.[9] The intensity of the YB luminescence increased after annealing, suggesting that the observed enhancement of the emission rate is due to the defects induced by annealing. For the as-deposited sample, the S value in the YB region was almost constant (0.462), but for the annealed sample, it increased from 0.494 to 0.528 in this energy range. Thus, we conclude that vacancy clusters in the subsurface region of the annealed sample were responsible to the observed enhancement of YB luminescence.

Figure 5 shows annealing behaviors of S for Ti-, Ni-, and Pt-deposited GaN with and without the metal layers. All measurements were made in the dark. For the samples with the metal layers, since the highest number of positrons were implanted into the metal layers at $E = 1.3$ keV, the S value at this energy reflects the annealing behaviors of vacancy-type defects in the metal layers. For Ti-deposited GaN, the S value shown in Fig. 5(a) increased with increasing annealing temperature, suggesting the agglomeration of vacancy-type defects in the Ti layer. The S value then started to decrease at 550 °C annealing. At the same annealing temperature, the S value for GaN [Fig. 5(b)] started to increase, which was due to the introduction of vacancy-type defects in GaN. Thus, we conclude that the shrinkage of vacancy size in the Ti layer correlates with the out-diffusion of atoms from GaN. In the annealing behavior of S for the Ti layer, the observed increase in S at 700 °C is an effect of defect introduction below the Ti layer.

For the Ni layer [Fig. 5(a)], the S value started to increase above 400 °C annealing, and decreased at 800 °C

annealing, which can be attributed to the agglomeration and dissociation of vacancy-type defects in the Ni layer. The former annealing temperature corresponds to the final recovery state of vacancies in deformed Ni.[10] Unlike in the case of Ti-deposited GaN, no increase in the S value was observed in Fig. 5(b). For Ni-based Schottky contacts, Ni nitride is known to form at as low as 200 °C.[3] Such an interlayer is thought to suppress atomic diffusion between Ni and GaN. For the Pt layer, the S value increased with increasing annealing temperature, suggesting the agglomeration of vacancy-type defects in Pt. The S value shown in Fig. 5(b) was almost constant, but larger than that for Ti- and Ni-deposited GaN below 700 °C. This suggests that the Pt-deposition increases the trapping fraction of positrons by defects just after deposition, but the Pt/GaN interface is very stable even after annealing at 700 °C. As discussed above, the defect trapping of positrons is suppressed by the presence of carbon in GaN. Because Pt could act as a catalyst to change the impurity concentrations below the Pt layer, the trapping rate of positrons could be increased by Pt deposition.

In summary, we used positron annihilation spectroscopy to study vacancy-type defects in metal- (Ti, Ni, and Pt) deposited GaN. We found that optically active vacancy-type defects were introduced below the Ti/GaN interface after annealing at 800 °C. The major defect species was identified as vacancy clusters such as $(V_{Ga})_m(V_N)_n$ (m = 3–5, n = 9 and 13). Charge transfer of those defects occurred under the illumination in the range between 2.0 and 2.7 eV, corresponding to YB in the PL spectrum. No detectable defects caused by Ni deposition were observed in GaN, which can be attributed to the interlayer which suppresses atomic diffusion between Ni and GaN. We have shown that the positron annihilation is sensitive to vacancy-type defects introduced by metal dispositions on GaN, meaning that this technique can be a useful tool for evaluating the degradation of metal contacts in GaN-based devices.

[1]S. W. Kaun, M. H. Wong, U. K. Mishra, and J. S. Speck, Semicond. Sci. Technol. **28**, 074001 (2013).
[2]B. J. Baliga, Semicond. Sci. Technol. **28**, 074011 (2013).
[3]D. J. Cheney, E. A. Douglas, L. Liu, C.-F. Lo, B. P. Gila, F. Ren, and S. J. Pearton, Materials **5**, 2498 (2012).
[4]F. Tuomisto and I. Makkonen, Rev. Mod. Phys. **85**, 1583 (2013).
[5]A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, E. A. Kozhukhova, S. J. Pearton, F. Ren, L. Lui, J. W. Johnson, N. I. Kargin, and R. V. Ryzhuk, J. Vac. Sci. Technol. B **31**, 011211 (2013).
[6]A. van Veen, H. Schut, J. de Vries, R. A. Hakvoort, and M. R. Ijpma, AIP Conf. Proc. **218**, 171 (1991).
[7]S. Ishibashi and A. Uedono, J. Phys. Conf. **505**, 012010 (2014).
[8]A. Uedono, S. Ishibashi, N. Oshima, and R. Suzuki, Jpn. J. Appl. Phys., Part 1 **52**, 08JJ02(2013).
[9]A. Uedono, T. Fujishima, Y. Cao, Y. Zhang, N. Yoshihara, S. Ishibashi, M. Sumiya, O. Laboutin, W. Johnson, and T. Palacios, Appl. Phys. Lett. **104**, 082110 (2014).
[10]A. P. Druzhkov, V. L. Arbuzov, and S. E. Danilov, Phys. Status Solidi A **205**, 1546 (2008).