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Defects in the Ti/GaAs system probed by monoenergetic positron beams

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Abstract. Defects in a Ti(96 nm)/GaAs specimen were probed by monoenergetic positron beams. From measurements of Doppler broadening profiles of the annihilation radiation and lifetime spectra of positrons, vacancy-type defects were found to be present in both the Ti layer and the GaAs substrate. In the GaAs substrate, a damaged region was present below the Ti/GaAs interface, and its width was about 100 nm. The lifetime of the positrons (336 ps) trapped by the vacancy-type defects in this region was close to that of divacancies, V_2 , while the characteristic value of the lineshape parameter S for such defects was smaller than that for V_2 . From these results, the major species of the defects in the region below the Ti/GaAs interface was identified as being divacancy–impurity complexes.

1. Introduction

Metal–GaAs field-effect transistors have been used in microwave communication devices and high-speed integrated circuits. The reliability and the stability of these devices are intimately related to controllable and high-yield metallization processes of metal/GaAs contacts. For Schottky contacts incorporating metal/GaAs systems, it is well known that interface states are inevitably present at the boundaries between the metals and the GaAs [1]. Many studies have been carried out with the aim of explaining the origin of the interface states [2, 3]. Another area of considerable interest is the interfacial reactions of the metal/GaAs system. Because Ti-based metallizations are frequently used to fabricate Schottky contacts, many studies of the Ti/GaAs system have been carried out [4–6]. During the formation of interface states or the interfacial reactions of the Ti/GaAs system, vacancy-type defects might play an important role, but information on such defects is limited at this stage.

The positron annihilation technique has become an established tool in the study of point defects in materials [7]. In condensed matter, a positron annihilates with an electron from the surrounding medium into two 511 keV γ -quanta. The motion of the positron–electron pair causes a Doppler shift in the energy of the annihilation photons. In a material containing vacancy-type defects, a freely diffusing positron may be localized in a vacancy-type defect by a Coulomb repulsion from ion cores. Since the momentum distribution of electrons in vacancy-type defects is different from that in the bulk, one can detect defects through

measurements of Doppler broadening profiles of the annihilation radiation. The change in the Doppler broadening spectrum is characterized by the lineshape parameter S , which is the ratio of the number of counts in the central region of the spectrum to the total number of counts [8]. When positrons are trapped by vacancy-type defects, the lifetime of the positrons increases because of a reduced electron density in such defects. Using high-energy positrons emitted from radioisotopes, vacancy-type defects in GaAs have been successfully studied [9–11]. The implantation profile of monoenergetic positrons can be adjusted to a restricted region of interest in the specimen by accelerating them to the desired energy [12]. Thus, measurements of the S -parameter as a function of the incident positron energy can provide depth profiles of the defects in the subsurface region. Ling *et al* [13] and Uedono *et al* [14] characterized metal/GaAs interfaces using monoenergetic positron beams. In these studies, Doppler broadening profiles were measured to detect defects in the metal/GaAs system. Since the relationship between the lifetimes of positrons and the species of vacancy-type defects has been established for typical semiconductors such as Si or GaAs [15], the defects can be identified from measurements of lifetime spectra of positrons. In the present study, we applied a pulsed monoenergetic positron beam in order to measure lifetime spectra of positrons for the Ti/GaAs specimen.

2. Experiment

The layer structure of the specimen used in the present experiment was Ti(96 nm)/GaAs/AuGeNi. A semi-insulating GaAs wafer grown by the liquid-encapsulated Czochralski (LEC) method was used as the substrate. Before the deposition of the metal layers, the substrate was chemically etched to remove natural oxide layers. An evaporated AuGe(13 wt%) eutectic (50 nm) with a Ni overlayer (13 nm) was alloyed at 450 °C under a N₂ atmosphere (60 s). Ti was deposited on GaAs/AuGeNi by the electron-beam evaporation method, where the thickness of the Ti layer was monitored by a silica glass subjected to the same evaporation conditions, and was determined to be 96 nm. After the deposition, the specimen was annealed at 300 °C under a N₂ atmosphere (45 min) to form the Schottky contact.

A monoenergetic positron beam line was used in the present experiment [16]. Doppler broadening profiles of the annihilation radiation were measured by a Ge detector as a function of the incident positron energy at room temperature. A spectrum with a total count of 1×10^6 was measured for each incident positron energy. The observed spectrum was characterized by the S -parameter, where the central region of the spectrum was defined as extending from 510.25 keV to 511.75 keV. A bias voltage, V_b , was applied to the GaAs substrate to accumulate positrons at the Ti/GaAs interface.

The observed relationship between the S -parameter and the incident positron energy, E , was analysed using the computer code ‘VEPFIT’ developed by van Veen *et al* [17]. The one-dimensional diffusion model of positrons is described by [12]

$$D_+ \frac{d^2}{dz^2} n(z) - \kappa_{eff}(z)n(z) + P(z, E) = 0 \quad (1)$$

where D_+ is the diffusion coefficient of the positrons, $n(z)$ is the probability density of the positrons at a distance z from the surface, $\kappa_{eff}(z)$ is the effective escape rate of the positrons from the diffusion process, and $P(z, E)$ is the implantation profile of the positrons. In equation (1), it was assumed that there was no electric field in the specimen. $n(z)$ can be obtained by numerical solution of equation (1) with boundary conditions which are suitable for the specimen. In the present work, the region sampled by the monoenergetic positrons

was divided into three blocks—the Ti layer, the damaged layer, and the GaAs substrate—where the boundary positions of the blocks were determined by the fitting. $\kappa_{eff}(z)$ is related to the concentration of defects, $C_d(z)$, by $\kappa_{eff}(z) = \lambda_b + \mu_d C_d(z)$, where λ_b is the rate of annihilation of positrons from the delocalized state, and μ_d is the specific positron trapping rate of the defect. The diffusion length of the positrons, $L_d(z)$, is given by

$$L_d(z) = \sqrt{D_+/\kappa_{eff}(z)}. \quad (2)$$

The observed S – E curve was fitted to the relation

$$S(E) = S_s F_s(E) + S_{Ti} F_{Ti}(E) + S_d F_d(E) + S_{GaAs} F_{GaAs}(E) \quad (3)$$

where S_s , S_{Ti} , S_d , and S_{GaAs} are the characteristic values of the S -parameter for the annihilation of positrons at the surface, in the Ti layer, in the damaged layer, and in the GaAs substrate, respectively. The fraction of positrons annihilating in the i th region, $F_i(E)$, is calculated using $n(z)$ and the rate of annihilation of positrons at z . Details of $P(z, E)$ were given elsewhere [18].

A pulsed monoenergetic positron beam line constructed at the Electrotechnical Laboratory was used to measure lifetime spectra of positrons [19]. The lifetime spectra were obtained by measuring the time interval between the timing signal derived electrically from the pulsing system and the annihilation γ -ray. For each lifetime spectrum, about 1×10^6 counts were accumulated, and E was fixed at 15 keV. The lifetime spectrum of positrons, $I(t)$, is expressed by

$$I(t) = \sum_{i=1}^n \lambda_i I_i \exp(-\lambda_i t) \quad (4)$$

where λ_i and I_i are the annihilation rate of positrons of the i th component and its intensity, respectively. The lifetime of the positrons, τ_i , is given by $1/\lambda_i$. The observed lifetime spectra of the positrons were analysed using the computer code ‘RESOLUTION’ [20] with a time resolution of about 300 ps.

3. Results and discussion

Figure 1 shows the S -parameter as a function of the incident positron energy for the Ti(96 nm)/GaAs specimen. The mean implantation depth of the positrons is shown below the horizontal axis in the figure, together with E . A plateau at $E = 1$ – 3 keV in the S – E curve is attributed to the annihilation of positrons in the Ti layer [14]. In figure 1, S for $E > 10$ keV increases on applying the bias voltage. The observed difference between the value of S for the specimen with and without the bias voltage can be attributed to the diffusion of positrons toward the Ti/GaAs interface from the GaAs substrate, and the resultant annihilation of positrons near the Ti/GaAs interface. Since an increase in S indicates the annihilation of positrons trapped by vacancy-type defects, the result obtained suggests the presence of a vacancy-rich region between the Ti layer and the GaAs substrate.

The lifetime spectra of positrons implanted at $E = 15$ keV were measured for the specimen with $V_b = 0, 10,$ and 300 V. The lifetime spectrum for the specimen without a bias voltage was decomposed into two components, and the others were analysed by assuming one annihilation mode. The derived lifetimes and their intensities are summarized in table 1. In table 1, the second lifetime, τ_2 , obtained for the specimen without a bias voltage is close to the lifetimes obtained for the specimen with the bias voltage. This means that the probability of annihilation of positrons with $\tau \simeq 336$ ps increases on applying the bias voltage. Since these lifetimes are longer than the lifetime corresponding to the annihilation of positrons

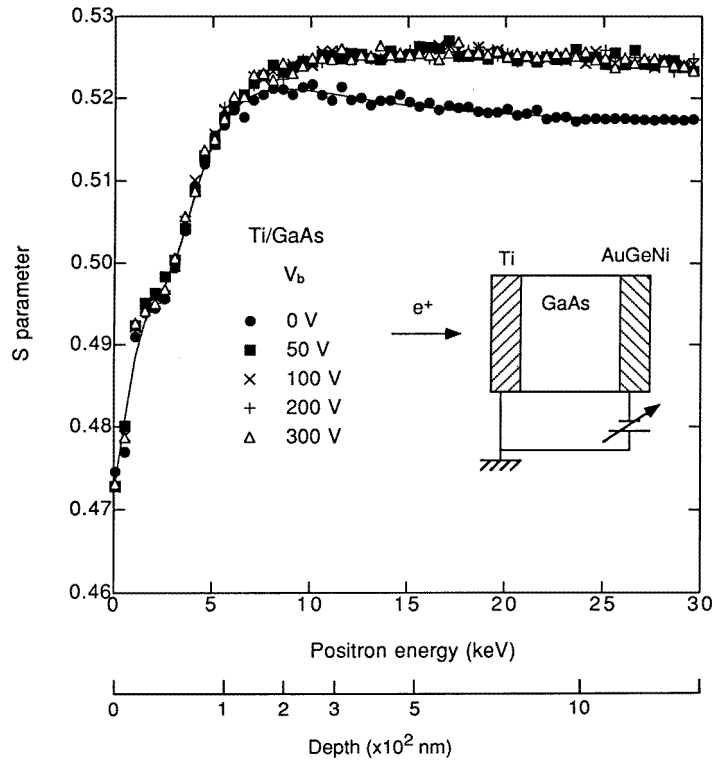


Figure 1. The S -parameter as a function of the incident positron energy for the Ti(96 nm)/GaAs specimen. The solid curve is a fit to the experimental data of equation (3). The derived parameters are summarized in figure 2. A schematic diagram of the experimental set-up is shown in the inset.

Table 1. The lifetimes and the intensities for the Ti(96 nm)/GaAs specimen. These values were obtained from the analysis of lifetime spectra of positrons with $E = 15$ keV.

V_b (V)	τ_1 (ps)	τ_2 (ps)	I_1 (%)
0	110(90)	331(7)	17(6)
10	333(2)	—	100
300	338(2)	—	100

from the delocalized state in GaAs (220–230 ps; references [21] and [22]) or that in Ti (148 ps; reference [23]), the present long-lived annihilation mode can be attributed to the annihilation of positrons trapped by vacancy-type defects. This conclusion agrees with that obtained from the measurements of Doppler broadening profiles. The lifetime spectra for the specimen with the bias voltage were satisfactorily analysed assuming one annihilation mode. This means that almost all of the positrons annihilate from the state trapped by vacancy-type defects. This also suggests that S for $E > 10$ keV for the specimen with the bias voltage is close to the characteristic value of S for the vacancy-type defects in the damaged layer (figure 1).

The S – E curve for the specimen without a bias voltage was fitted using equation (3).

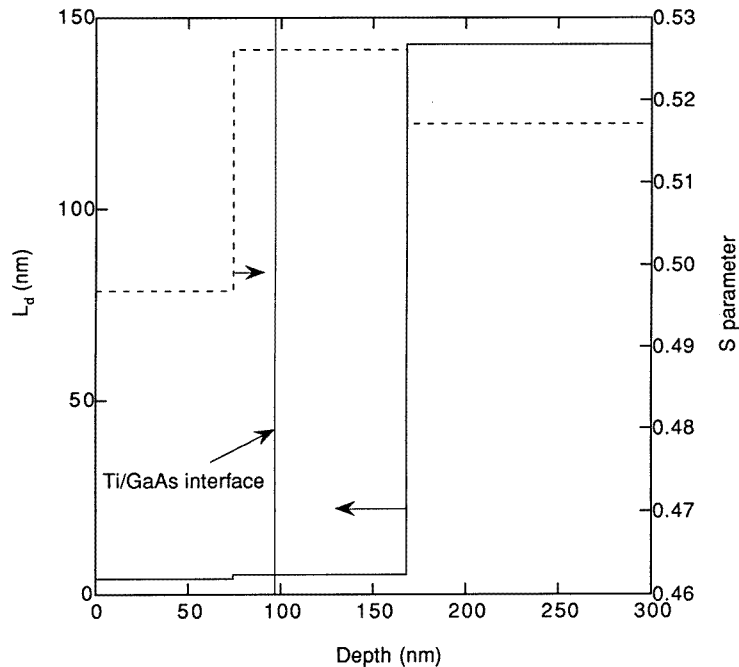


Figure 2. The depth profiles of the S -parameter and the diffusion length of the positrons for the Ti(96 nm)/GaAs specimen. The vertical line shows the location of the Ti/GaAs interface.

S_d was fixed as the averaged value of S at $E = 13\text{--}18$ keV for the specimen with the bias voltage. The diffusion length of the positrons in the GaAs substrate was fixed as equal to that for the semi-insulating LEC-GaAs specimen without a Ti layer (143 nm) [24]. Although the diffusion length of the positrons in the damaged layer, $L_{d(d)}$, was not uniquely determined, it was below 10 nm. Thus, $L_{d(d)}$ was fixed as 5 nm. This means that almost all of the positrons annihilate from the trapped state in the damaged region [16]. The depth profiles of S and L_d obtained are shown in figure 2, where the location of the Ti/GaAs interface is also shown. The diffusion length of the positrons in the Ti layer, $L_{d(\text{Ti})}$ (3.9 nm) was far shorter than the typical value of L_d for defect-free metals ($L_{d(\text{free})} = 100\text{--}200$ nm; reference [25]). From equation (2), the decrease in L_d can be attributed to the increase in the concentration of defects. The fraction of positrons trapped by defects in the Ti layer, F_d , can be calculated to be 1 using the relation [16] $F_d = 1 - (L_{d(\text{Ti})}/L_{d(\text{free})})^2$. Thus, the value of S_{Ti} obtained is the characteristic value of S for the annihilation of positrons from the trapped state by defects in the Ti layer. Since Ti is an excellent getter, impurities such as oxygen or hydrogen atoms might exist in the Ti layer, and could affect the positron annihilation parameters. For metals, the trapping of positrons by vacancy-type defects is known to saturate at $C_d > 10^{-6}\text{--}10^{-5}$ [8]. In the present experiments, since the Ti layer was deposited by the electron-beam evaporation method, C_d for the Ti layer is expected to be high. Thus, the major response of the positron annihilation parameters for the Ti layer is likely to be attributable to the annihilation of positrons trapped by vacancy-type defects.

In figure 2, there seems to be a damaged region in both the Ti layer and the GaAs substrate. Ling *et al* [13] analysed the S - E curves for Au/GaAs and Al/GaAs using a fitting model similar to that used in the present work. They also found a damaged region

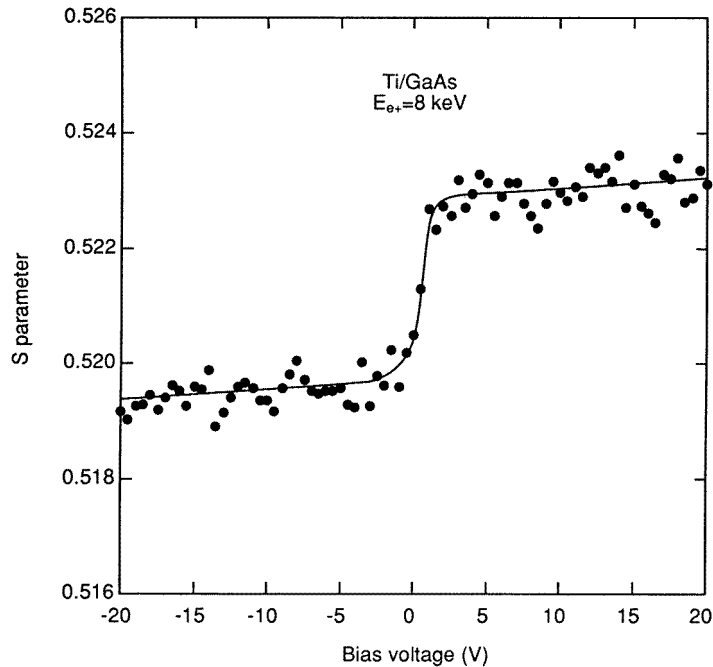


Figure 3. The relationship between the S -parameter at $E = 8$ keV and the bias voltage for the Ti(96 nm)/GaAs specimen.

to be present between the metal layer and the GaAs substrate. According to their studies, the damaged region was attributable to the intermixing of atoms and the resultant formation of new phases. In the present experiment, however, alloyed layers with widths of about 100 nm are unlikely to be introduced by 300 °C annealing [4, 5]. In order to interpret the annihilation characteristics of positrons in the damaged region in more detail, the change in the Doppler broadening profiles on applying the bias voltage was studied as follows. Figure 3 shows the S -parameter measured at $E = 8$ keV as a function of the bias voltage. The observed S - V_b curve can be associated with the change in the band structure of the GaAs substrate caused by applying the bias voltage. In order to increase the statistical accuracy, the Doppler broadening profiles measured for $V_b < -5$ V and those measured for $V_b > 5$ V were summarized, respectively. Figure 4 shows the profile measured with the high bias voltages ($V_b > 5$ V), and the difference between the two profiles, where the profile measured with low bias voltages ($V_b < -5$ V) was subtracted from that measured with high bias voltages. The horizontal axis shows the energy shift of the γ -rays from 511 keV, ΔE_γ .

Measurements of Doppler broadening profiles are equivalent to measurements of the angular correlation of annihilation radiation (ACAR) [7]. From measurements of ACAR spectra for Ge, Shullman *et al* [26] observed a pronounced minimum in the low-momentum region in the spectra. For semiconductors such as Ge and Si, p atomic orbitals on nearest-neighbouring sites are inverted with respect to each other to form covalent bonds. Chiba and Akahane [27] suggested that such a configuration of atomic orbitals suppresses the contribution to the momentum density from these sites, and introduces the dip observed in the low-momentum region. For a Si specimen containing divacancies, this dip was found

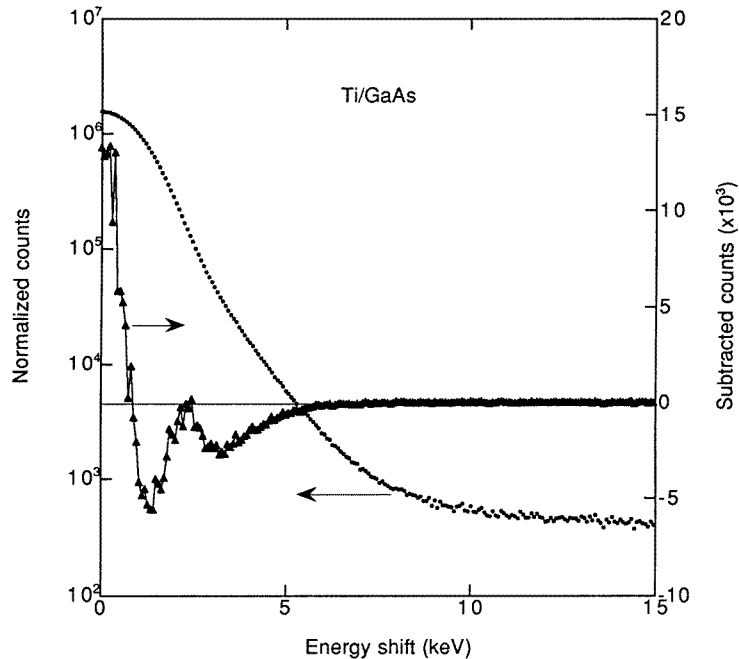


Figure 4. The Doppler broadening profile measured for $V_b > 5$ V, and the difference between the two Doppler broadening profiles, where the profile measured for $V_b < -5$ V was subtracted from that measured for $V_b > 5$ V. During the measurements, the incident positron energy was fixed at 8 keV.

to disappear [28]. This was attributed to the revival of the bands due to the lowering of the crystal symmetry at defects.

In figure 4, it can be seen that the profile measured for the high bias voltages mainly consists of narrow and broad components. The broad component clearly observed for $\Delta E_\gamma > 2.5$ keV corresponds to the annihilation of positrons with core electrons. The narrow component observed for $\Delta E_\gamma < 2.5$ keV is identical to the momentum distribution of positron–electron pairs discussed above. According to the above discussion, for the subtracted profile, the positive values for $\Delta E_\gamma < 1$ keV are attributable to the lowering of the crystal symmetry due to the trapping of positrons by vacancy-type defects. The negative values for $2.5 \text{ keV} < \Delta E_\gamma < 6 \text{ keV}$ can be attributed to the decrease in the probability of annihilation of positrons with core electrons in vacancy-type defects. The derived subtracted profile is a typical one for the annihilation of positrons trapped by vacancy-type defects in semiconductors [29, 30]. The Doppler broadening profile corresponding to the annihilation of positrons in alloyed layers is expected to be very different from that for GaAs. If the Doppler broadening profile measured at the high bias voltages incorporates the annihilation mode of the positrons in the alloyed layers, the subtracted profile is unlikely to represent a typical one corresponding to the trapping of positrons by vacancy-type defects in semiconductors. Thus, the defects in the damaged region can be identified as being vacancy-type defects in the GaAs substrate. The location of the damaged region, therefore, is considered to be below the Ti/GaAs interface.

The derived lifetime (336 ps) corresponding to the annihilation of positrons trapped by the vacancy-type defects is longer than the lifetimes of positrons trapped by monovacancies

but close to those of positrons trapped by divacancies [15, 21, 22]. Thus, the open size of the vacancy-type defects is considered to be close to that of divacancies. By using high-energy positrons emitted from ^{22}Na , Shan *et al* [31] reported that the lifetime of positrons at Al/GaAs interfaces was about 380 ps. According to their study, this lifetime value was attributable to the annihilation of positrons trapped by microvoids or vacancy clusters at the interface. This concept of the presence of vacancy-type defects below the metal/GaAs interface is in good agreement with the conclusion reached in the present work.

The ratio of the characteristic value of S for the annihilation of positrons trapped by monovacancies to that for the annihilation of positrons from the delocalized state was estimated to be about 1.02 [9, 32]. In the present experiment, S_d/S_{GaAs} (1.018) is close to this value, but the open size of the defects estimated using the lifetime of positrons is larger than that of monovacancies. For the annihilation of positrons trapped by vacancy–impurity complexes in Si, S was decreased by the presence of impurities such as oxygen and fluorine [33, 34]. Thus, in the present experiment, S_d might be decreased by the presence of impurities. One of the candidate groups for such impurities is Ti atoms diffused from the Ti layer. Since the native oxide layer is considered to be present at the surface of the GaAs substrate before the deposition of the Ti layer [35], oxygen atoms also constitute a candidate group. In summary, vacancy-type defects are present in both the Ti layer and the GaAs substrate. The damaged region in the GaAs substrate is present below the Ti/GaAs interface, and its width is about 100 nm. The open size of the defects in the GaAs substrate is close to that of the divacancies, and they are likely to be coupled with impurities.

Spicer *et al* [3] suggested that one origin of the Fermi-level pinning at metal/GaAs contacts is an As atom located at a Ga site. According to their discussion, the observed vacancy-type defects in the present work are not directly related to the Fermi-level pinning. However, since the vacancy-type defects near the interface act as sinks or sources for excess As or Ga, such defects are considered to play an important role during the deposition of metal layers. Tersoff [2] explained the Fermi-level pinning using the metal-induced gap-state model. According to this model, electron wave functions of metals decay into semiconductors and give rise to interface states within the semiconductor band gap. Because the defects could affect the band structure of semiconductors, information on the defects below the Ti/GaAs interface can contribute to such an approach.

4. Conclusion

We have studied the defects in the Ti/GaAs system using monoenergetic positron beams. Doppler broadening profiles of the annihilation radiation were measured as functions of the incident positron energy for a Ti(96 nm)/GaAs specimen. Lifetime spectra of positrons were also measured using a pulsed monoenergetic positron beam. From measurements of the S – E curves for the specimen with and without the bias voltage, the damaged region was found to be present between the Ti layer and the GaAs substrate. The characteristic value of S for the annihilation of positrons in the damaged region was larger than that for the Ti layer or the GaAs substrate. This suggests that the positrons implanted into the damaged region annihilate from the state trapped by vacancy-type defects. The Doppler broadening profile corresponding to the annihilation of positrons in the damaged region showed the typical form for annihilation of positrons trapped by vacancy-type defects in semiconductors. From the analysis of the S – E curve for the specimen without a bias voltage, the damaged region was found to be mainly present below the Ti/GaAs interface, and its width was about 100 nm. Thus, it was proposed that the defects in the damaged region are vacancy-type defects in the region below the Ti/GaAs interface. From measurements

of the lifetime spectra of positrons, the open size of the vacancy-type defects was found to be close to that of the divacancies. However, the characteristic value of S for these defects was smaller than that for divacancies. Thus, the defects are likely to be coupled with impurities such as Ti or oxygen atoms. The present investigation shows the potential of positrons for use as a nondestructive probe for the study of process-induced defects in metal/semiconductor systems.

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